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Frontispiece.

CHEMICAL AND PHYSICAL CHARACTERISTICS OF PHILIPPINE COAL.

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The uniformity in the composition of most Philippine coals,[1] barring diluents, water, ash, and sulphur, suggests that all were bedded under about the same conditions. This idea is substantiated by the fact that the deposits correspond geologically, although occasionally some are improved by geologic compression of the strata or certain other local peculiarities. The deposits considerably resemble black lignite, but are generally much superior to ordinary lignite. A few deposits have a brownish color and show a woody structure; however, in general they are bright and shiny, much resembling bituminous coal, although with a slightly lower calorific value. The name "subbituminous" best describes the average Philippine variety, since it conveys the most accurate idea of its nature and value. I have investigated samples of one coal from the Zamboanga Peninsula which shows 4.89 per cent of diluents (2.27 per cent moisture and 2.62 per cent ash) and a fixed carbon content of 88.53 per cent, indicating a semianthracite. Philippine coals as a rule are noncoking. One authentic sample of a seam from the Island of Cebu gives a coke which appears to be of good quality. The seam is not over 60 centimeters thick, and it is possible that the same

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[1] Cox, Alvin J., *This Journal*, Sec. A (1909), 4, 193.

geologic conditions which produced the coking coal render a continuous seam improbable. On the other hand, this seam is an encouragement to prospectors to seek in the deeper beds for good, coking coal in regular seams, for a supply of coke is much needed in the smelting of the iron and copper which occur in the Islands.

I have investigated the quality and means of utilization of the coal from as many representative sources as could be obtained. The quality of Philippine coal is shown by the following representative analyses and calorific values made by the Bureau of Science of samples collected during the past year:

TABLE I.—*Representative analyses and calorific values of Philippine coal.*

Number.	Source.	Proximate analyses.[a]							
		Mine sample.				Air dried.			
		Water.	Volatile combustible matter.	Fixed carbon.	Ash.	Water.	Volatile combustible matter.	Fixed carbon.	Ash.
		Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
1	Polillo	9.01	42.61	43.39	4.99	3.75	45.08	45.90	5.27
2	.....do	8.28	41.53	46.31	3.88	3.76	43.58	48.60	4.06
3	.....do	6.25	43.15	47.21	3.39	5.17	43.65	47.75	3.43
4	.....do	10.57	41.33	45.99	2.11	4.41	44.18	49.15	2.26
5	.....do	8.35	42.88	45.88	2.89	4.69	44.59	47.71	3.01
6	Liguan, Batan					7.05	37.43	49.10	6.42
7	.....do					6.37	37.14	53.49	3.00
8	.....do					6.93	36.30	53.20	3.57
9	East Batan	21.56	34.32	38.04	6.08				
10	.....do					16.95	35.83	36.98	10.24
11	.....do	22.70	33.75	38.76	4.79				
12	.....do	19.54	34.39	34.75	11.32				
13	.....do					19.12	32.64	33.46	14.78
14	.....do	20.92	33.28	36.10	9.70				
15	Bulalacao, Mindoro	27.77	37.18	27.59	7.46	17.57	42.43	31.49	8.51
16	Comansi, Cebu	9.01	43.46	43.18	4.35	7.49	44.18	43.90	4.43
17	Camujamayan Valley, Cebu	23.18	46.40	25.84	4.58	17.13	50.05	27.88	4.94
18	.....do	17.24	44.13	33.87	4.76	13.67	46.04	35.33	4.96
19	.....do	13.88	40.97	41.74	3.41	12.49	41.63	42.41	3.47
20	Compostela, Cebu	9.43	40.14	47.51	2.92	8.10	40.73	48.21	2.96
21	Sibuguey Bay, Mindanao	6.81	45.45	45.92	1.82	5.32	46.17	46.65	1.86
22	Margossa Tubig, Mindanao					2.25	6.83	87.62	3.30

[a] For other and earlier analyses of Philippine coal see Cox, A. J., *This Journal, Sec. A* (1906), 1, 397; (1907), 2, 41; (1908) 3, 301; (1909) 4, 171. Analyses Nos. 6 to 14 were made by the "smoking-off method." *This Journal, Sec. A* (1907), 2, 41. The empirical methods usually employed are not applicable to many of the Philippine coals, owing to certain peculiarities of the latter. The analyses as carried on by the "official method," *Journ. Am. Chem. Soc.* (1899), 21, 1116, often indicate Philippine coal to be of a much poorer quality than is actually the case.

TABLE I.—*Representative analyses and calorific values, etc.*—Continued.

Number.	Source.	Ultimate analyses and calories by calorimeter of the air-dried samples.							
		Hydro-gen.	Carbon.	Nitro-gen.	Oxy-gen.	Sul-phur.	Ash.	Main calo-ries.a	Available heating value.
		Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Calories.
1	Polillo			1.52		0.49	5.27	6,967	6,589
2	----do----	5.54	70.47	1.59	18.02	0.32	4.06	7,152	6,775
3	----do----			1.70		0.67	3.43	6,933	6,542
4	----do----			1.61		0.71	2.26	7,182	6,794
5	----do----			1.54		0.21	3.01	7,301	6,910
15	Bulalacao, Mindoro	5.87	52.60	0.96	29.52	2.54	8.51	5,363	4,959
16	Comansi, Cebu	5.11	66.18	1.72	20.16	2.40	4.43	6,600	6,248
17	Camujamayan Valley, Cebu	4.81	52.82	1.55	36.04	0.34	4.94	4,819	4,428
18	----do----			1.59		0.40	4.96	5,580	5,190
19	----do----			1.64		0.65	3.47	6,135	5,761
20	Compostela, Cebu	5.72	66.46	2.10	22.34	0.42	2.96	6,779	6,424
21	Sibuguey Bay, Mindanao	5.44	70.20	1.73	20.34	0.43	1.86	7,071	6,751

a In the usual determination of the calorific value of a fuel in a calorimeter, the products are cooled to the ordinary temperature and the result, therefore, is higher than can ever be realized in ideal practice, where the resulting gases always leave the flues at a temperature above 100°. Since the object of the determination of the calorific value of a fuel is to show its technical worth, I always have calculated the results on Philippine fuels on the assumption that the moisture present and the water formed during the combustion remain as steam at 100°, *i. e.*, I have made a water correction by subtracting 6 calories for each per cent of water. Some mechanical engineers do not make this correction and, therefore, obtain a result from 5 to 8 per cent too high; in order that my results may be comparable in all cases I have decided to give, also, the uncorrected results under the caption "Main calories."

For the purposes of comparison and to indicate the class of coal with which Philippine coal must compete, I have segregated in Table II representative analyses and calorific values of ships' cargoes of coal arriving in Manila which were sampled and analysed from December, 1910, to April, 1911, and, in Table III, I have given certain other coals which have the possibility of a market in the Philippines. Most of the analyses were made by F. B. Beyer.

TABLE II.—Selected analyses which represent the approximate average of each variety of coal which has arrived in Manila Harbor since December 1, 1910.

[Numbers, except as otherwise indicated, represent per cent.]

	Japan: Miike lump.	Japan: Miike nut.	Japan: Moji Tagawa 1 lump.	Japan: Moji Tagawa 2 lump.	Japan: Moji Yamano lump.	Japan: Moji Hondo lump.	Japan: Moji Umi lump.	Japan: Karatzu Ochi lump.	Japan: Maunoura 3 inch lump.	Japan: Iwaya lump.	Australia: New Castle best coal.	Australia: New Castle "Best screened ed. coal."	Australia: New Castle "Best screened ed."	Australia: New Castle Seeham "Best screened ed."	Australia: New Castle Browns Duckenfield Mer-thyr.	Borneo: La-buan.	China: Loco lump.
Per cent of fine coal (through 1¼-inch mesh)	68.00	97.71	23.40	76.50	40.50	46.40	30.60				24.00	20.70					
Per cent of slack (through ¼-inch mesh)	23.75	19.64	8.10	10.80	12.60	20.00	6.30				5.40	8.10					
Number of tons in cargo	2,385	2,740	800	1,450	1,000	500	100	3,400			3,632	3,734		3,830	5,021	1,791	
Proximate analysis:																	
Moisture	0.36	0.43	2.74	2.44	1.83	2.45	1.94	2.82	3.38	1.76	1.51	2.08		2.56	2.41	6.14	0.88
Volatile combined matter	39.40	41.45	39.01	40.41	38.85	38.92	40.27	39.65	38.84	40.96	35.04	34.37		35.08	33.69	43.76	27.27
Fixed carbon	46.51	47.59	47.32	46.83	43.39	46.75	45.03	47.59	44.73	48.69	52.56	53.11		51.96	53.65	46.21	49.62
Ash	13.67	10.53	10.93	10.32	15.93	11.88	12.16	10.44	13.05	8.59	10.89	10.44		10.40	10.25	3.89	22.28
Total	99.94	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00		100.00	100.00	100.00	100.00
Sulphur (separately determined)	3.00	2.90	0.29	0.72	1.61	0.36	0.52	1.01	1.51	0.78	0.14	0.53		0.51	0.96	0.48	1.14
Color of ash	(a)	(a)	(b)	(b)	(a)	(b)	(b)	(b)	(e)	(b)	(b)	(b)		(b)	(c)	(d)	(a)
Coking quality	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)		(f)	(f)	(g)	(f)
Available heating value in calories by calorimeter	7,107	7,402	6,719	6,460	6,403	6,343	6,638	6,627			6,740	6,695		6,711	6,640	6,508	
Analysis of ash:																	
Silica (SiO_2)	36.41	38.20			50.25	46.84	47.44	41.48			46.68	53.04		57.48	45.95	34.72	
Alumina (Al_2O_3)	18.45	16.06			27.07	32.19	27.23	25.41			37.59	31.02		30.22	24.96	35.79	
Ferric oxide (Fe_2O_3)	5.45	5.06	1.79	5.36	8.09	4.36	6.22	5.23			7.47	7.78		3.74	16.58	11.20	

Lime (CaO)	18.41	16.09	4.75	5.25	6.05	7.69	7.64	10.37		2.95		1.97	3.55	3.35	3.76
Magnesia (MgO)	2.51	2.59	0.74	0.47	0.42	0.45	0.70	3.30		1.46		0.33	1.50	0.64	3.97
Sulphuric anhydride (SO_3)	12.64	8.40	0.20	0.16	1.84	1.97	1.70	4.70		nil		0.81	0.50	3.07	2.07
Phosphorous Pentoxide (P_2O_5)	0.50	0.93	0.85	0.29	0.19	0.05	Trace			0.37			0.30	1.98	0.13
Loss on ignition	3.03	9.57	6.46	5.93	2.48	4.72	6.46	7.44		2.00		3.76	2.23	0.90	7.26
Alkalies and undetermined	2.60	3.10	h3.81	h4.26	3.61	1.73	2.61	1.07		1.43		1.69	0.03	h2.79	1.10
Total	100.00	100.00			100.00	100.00	100.00	100.00		100.00		100.00	100.00	100.22	100.00

a Gray.   b Light brown.   c Reddish gray.   d Reddish brown.   e Light reddish brown.   f Coking.   g Noncoking.   h Alkalies only.

TABLE III.—Analyses of certain coals which have the possibility of a market in the Philippines.

	Cowie Harbor, British North Borneo				Labuan, Borneo				Brooketon, Sarawak, Borneo			
	Mine sample.	Air dried.	Mine sample.	Air dried.	Mine sample.	Air dried.	Mine sample.	Air dried.	Mine sample.	Air dried.	Mine sample.	Air dried.
Proximate analysis:												
Moisture	4.34	1.01	5.43	0.80	6.12	4.06	6.35	3.47	12.38	9.80	13.06	9.92
Volatile combustible matter	41.25	42.68	40.44	42.42	43.53	44.49	45.64	47.04	39.52	40.68	39.69	41.13
Fixed carbon	38.10	39.42	39.88	41.83	48.70	49.77	44.18	45.54	44.56	45.87	44.46	46.07
Ash	16.31	16.89	14.25	14.95	1.65	1.68	3.88	3.95	3.54	3.65	2.79	2.88
Ultimate analysis:												
Hydrogen		5.42				6.09		6.16		5.81		
Carbon		56.14				70.63		69.61		62.58		
Nitrogen		1.13				1.57		1.53		1.09		
Oxygen		15.55				19.74		18.30		26.18		
Sulphur		4.87				0.29		0.45		0.74		
Ash		16.89				1.68		3.95		3.65		
Available heating value in calories by calorimeter		6,311		6,576		6,640		6,592		5,749		5,816

As is shown by the above analyses and following tests, the fuel value of Philippine coal is usually somewhat less than that from Australia, but equal to that from Borneo and from many Japanese mines, which it strongly resembles.

Although coal occurs abundantly throughout the Philippine Archipelago, it has been used as a fuel from only a very few mines. It has been employed on small vessels plying along the coast with fairly satisfactory results as regards its steam-making properties, but, largely owing to the undeveloped condition of the mines and the difficulty of transportation, it has come into very little competition with the coal imported from Japan, Australia, and other points at a great distance. With Manila's good dock facilities, if we had an abundant, available supply of good, cheap coal, many commercial industries could be developed and increased.

Complaints of Philippine coal are occasionally heard, but usually from individuals with little knowledge of the product itself and who have paid less attention to the best means of utilizing it. How best to utilize the coal deposits of this country is a question which has long attracted attention and at the present time, owing to the limited use of Philippine coal, can not be considered as solved. Tests of Batan coal from the military mines were made on the United States Army Transports *Chukong, Sacramento,* and *Palawan* in 1904, and the reports in each case were favorable. The tenor of all was that the coal was easily fired, it burned well, the amount of soot was comparatively small, there was no great quantity of smoke, the ash and refuse content was low, and there was no clinker. It was not necessary to clean the fires oftener than once in eight hours.

A trial of the commercial value of coal from the Island of Polillo was made at the Philippine Cold Storage and Ice Plant in 1906, and complete data of the test were kept.[2] The test was as satisfactory as possible under the existing conditions; the results exceeded the anticipations of those in charge of the test and seemed to indicate "its equality with many other coals on the Manila market." However, the grates were not adapted to the fuel and much inconvenience was experienced because the decrepitated coal passed through the grate with the ash. Toward the end of the test, this ash was burned again, and after the second burning the analyses by the Bureau of Science

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[2] *Far Eastern Review* (1906), 2, 223.

showed it to contain 62.6 per cent of combustible matter. No comparative tests were made with other coals.

In 1908, I determined the steaming value of available Philippine coals as measured by kilograms of water evaporated per kilogram of fuel when used under a boiler, as compared with the foreign coals offered on the market in this Archipelago.[3] Careful and complete records have been preserved of each test and, therefore, it should be possible for engineers to determine from the data which are given, whether or not the conditions were those best suited to the coal under examination, and when a price is established for these coals, the results will form a basis of comparison not only as to the water evaporated per kilogram of fuel, but also in regard to the water evaporated per peso of fuel cost. In commercial operations the all-important question is to find the fuel which will run a plant with the least financial outlay.

As the supply of material has generally been limited, except in the case of Australian coal which has always been the fuel of the Bureau of Science, only a limited amount of preliminary experimenting could be done to determine the best practice in regard to firing and to gain information regarding the fuel before beginning the test. An engineer always needs experience with a coal to burn it in the most effective manner. Promiscuous tests of coals made under different conditions are not at all comparable, for it is impossible to discover whether the variations are due to the fuel, the apparatus, or the manipulation. In the following tests, many factors have been eliminated by using the same plant[4] and the same personnel; the others have been carefully controlled by using the same apparatus and maintaining all manipulations and general conditions as nearly constant as possible. The fuels were all fired in the gridiron-grate furnace of the Bureau of Science, for which the usual fuel is Australian coking coal; in fact it is especially suited to and designed for the consumption of coal of this class. A furnace with a short firebox, planned for a high-grade, steaming coal, which burns with a short, hot, smokeless flame, is entirely unsuited to Philippine coal. In the following tests, the advantage in this regard was in favor of the Australian coal. The results of the tests are shown in Table IV.

[3] *This Journal, Sec. A* (1908), 3, 301. The headings "Oxygen" of the fourth and "Nitrogen" of the fifth vertical columns, respectively, in the Table on page 313 should be interchanged.

[4] The losses through radiation and conduction do not vary greatly for any given installation.

TABLE IV.—*Steaming tests of Philippine and other coals.*

[The black-faced figures over columns are code numbers of the American Society of Mechanical Engineers.]

No. of test.	Source of coal.	Commercial size of coal.	Duration of trial. (2) Hrs. min.	Avg. steam pressure, per sq. centimeter (Kilos)	Avg. steam pressure, per sq. inch (11) (Pounds)	Avg. temp. of escaping flue gases. (21) °C.	Proximate analysis — Fixed carbon. (32)	Proximate analysis — Volatile combustible matter. (33)	Proximate analysis — Moisture. (34)	Proximate analysis — Ash. (35)	Calorific value of coal as fired. (Calories)	Total amount fired. (25) Kilos	Total ash and refuse. (28) Kilos	Clinker in ash and refuse. (29) Per ct.	Ash and refuse referred to dry coal. (31) Per ct.
	Australia:														
1	Westwaldsend [e]	Lump and slack	7 00	7.416	105.5	360	50.94	34.23	2.80	12.08	6,614	1,474.0	196.9	25.1	13.73
2	Do [e]	...do	7 00	7.249	103.1	364	50.94	34.23	2.80	12.08	6,614	1,497.0	198.2	29.3	13.62
3	Do	Selected lump	7 00	7.797	110.9	378	52.43	36.64	1.74	9.19	6,933	1,288.8	152.4	20.0	12.57
4	Lichzow Valley	Lump and slack	7 00	7.906	112.5	391	52.62	32.47	2.11	12.80	6,987	1,174.4	197.3	None[d]	17.16
5	Do [e]	...do	6 45	7.571	107.7	400	52.62	32.47	2.11	12.80	6,987	1,334.5	207.3	None[d]	15.86
	Japan:														
6	Yoshintani (Karatsu), Kiushu Island	Lump	7 00	7.831	111.4	383	48.83	37.53	1.83	12.31	6,691	1,684.0	253.1	39.8	15.78
7	Yubari (Hokkaido Province)	...do	5 00	7.750	110.2	395	42.69	45.60	1.32	10.39	7,127	1,072.9	168.7	33.6	15.96
8	Borneo, Labuan	Pea to lump	7 00	6.894	97.2	377	50.65	41.85	5.43	2.67	6,664	1,791.0	115.2	11.8	6.81
9	Do [e]	...do	6 40	7.365	104.7	398	50.55	41.35	5.43	2.67	6,664	1,791.0	169.8	None.	6.48
	Batan Island:														
10	Military reservation [f]	Lump and slack	7 30	7.417	105.7	414	45.51	40.76	5.18	8.55	6,079	1,947.8	361.9	17.9	19.43
11	Do	...do	7 05	7.761	110.4	310	49.41	38.26	5.88	6.45	6,298	1,587.6	326.1	2.6	21.84
12	Do	...do	7 00	7.761	110.4	334	50.30	38.99	5.87	4.84	6,359	1,562.6	269.0	3.2	18.27
13	Military reservation, seam No. 4	Lump	7 00	7.656	108.9	414	51.75	39.15	6.08	3.02	6,584	1,572.5	201.5	9.0	13.66
14	Do [e]	...do	6 50	7.862	111.8	392	51.68	39.80	6.05	2.57	6,610	1,404.3	162.9	7.8	12.35

15	Betts'	Lump and slack.	4	00	4.471	63.6	406	38.33	36.56	18.03	7.08	4,647	1,134.0	87.3	8.0	9.40
16	Do	...do...	7	00	7.375	104.9	440	34.86	36.50	18.61	10.03	4,560	2,313.4	281.5	7.8	14.95
17	Cebu, Comansi	Lump	5	80	7.547	107.3	390	46.30	37.93	10.01	5.76	6,071	1,227.4	70.8	None.	6.41
18	Do	...do...	7	80	7.706	109.6	342	46.27	37.95	9.94	5.84	6,089	1,566.0	99.3	None.	7.08

[a] Mostly analyzed by H. S. Walker after the method of Cox, This Journal, Sec. A (1907), **2**, 41.

[b] This does not include the ash carried over the bridge wall.

[c] This is the laboratory fuel furnished by the Bureau of Supply. It is "double-screened and picked twice." It was purchased on Circular Proposal No. 248, at a contract price, delivered in Manila, and piled in the coal sheds and yards of the Civil Government at 10.75 pesos (5.375 dollars) per ton of 2,240 pounds.

[d] About 4 per cent of a soft incipient clinker which falls to pieces in dropping from the door of the furnace.

[e] This test shows the personal variation in firemen. A new man was put on, he could not keep his fire regular and the result was a somewhat low evaporation and at times high chimney temperature and low steam pressure.

[f] This coal does not represent the vein, for it had evidently lain in the tunnel where it had become water-soaked and considerably silted over. The ash content and clinker-forming ability are therefore high as compared with the run of this coal. It was very difficult to obtain an accurate laboratory sample. The ash shown by the chemical analysis is considerably less than that of the coal actually fired.

[g] In the use of this fuel, the coal on the grate was not disturbed from start to finish. It was alternately semicoked and spread-fired, and the result is more complete combustion, lower chimney temperature, and greater evaporation.

COX.

TABLE IV.—*Steaming tests of Philippine and other coals*—Continued.

[The black-faced figures over columns are code numbers of the American Society of Mechanical Engineers.]

No. of test	Source of coal	Commercial size of coal	Duration of trial [2]	Analysis of ash.				The coal, equivalent to the combustible material in the total refuse.	Per-centage of the coal as fired actually consumed.	Water fed to boiler.		Equivalent evaporation of water from and at 100°C.		Efficiency of boiler including grate, based on the chemical analysis.
				Fixed carbon.	Volatile combustible matter.	Moisture.	Ash.			[57]	[58] Equivalent from and at 100°C.[a]	[69] Per kilo of coal as fired.	Per kilo of coal actually consumed[b] of coal as fired.	[73]
			Hrs. min.					*Kilos.*		*Kilos.*				*Per ct.*
Australia:														
1	Westwaldsend[c]	Lump and slack	7 00	27.50	1.00	None.	71.50	58.7	96.02	8,961.5	10,538	7.160	7.446	57.99
2	Do[c]	...do	7 00	25.40		None.	74.60	49.1	96.71	8,875.0	10,492	6.970	7.206	56.53
3	Do	Selected lump	7 00	21.41	2.19	0.13	76.27	86.3	97.06	8,045.0	9,453	7.661	7.894	58.36
4	Lichzow Valley	Lump and slack	6 00	20.92	1.57	0.26	77.25	51.7	95.59	6,700.0	7,862	6.694	7.003	51.40
5	Do[d]	...do	6 45	19.68	1.44	0.20	78.68	51.0	96.18	7,317.5	8,579	6.429	6.684	49.36
Japan:														
6	Yoshintani (Karatsu), Kiushu Island	Lump	7 00	14.00	1.29	0.22	84.49	72.0	95.60	6,844.0	8,055	4.980	5.157	39.53
7	Yubari (Hokkaido Province)	...do	5 00	34.05	8.24	0.44	57.27	57.2	94.67	6,102.0	7,163	6.652	7.058	50.30
8	Borneo, Labuan	Pea to lump	7 00	51.98	7.89	1.79	38.34	71.5	96.01	8,290.0	9,734	5.435	5.661	48.75
9	Do	...do	6 40	52.51	7.16	2.90	37.43	77.4	95.68	8,084.0	9,505	5.307	5.546	42.72
Batan Island:														
10	Military reservation[e]	Lump and slack	7 30	65.50	7.60	3.80	23.11	189.0	90.30	7,691.0	9,058	4.650	5.148	41.04
11	Do	...do	7 05	65.48	5.18	2.79	25.85	286.6	81.94	5,883.0	6,853	4.317	5.268	37.62
12	Do	...do	7 00	71.95	6.16	2.23	20.27	229.0	85.34	5,953.0	6,994	4.476	5.245	37.76
13	Military reservation, seam No. 4	Lump	7 00	65.46	7.93	2.20	24.41	179.5	88.58	8,568.0	10,064	6.400	7.225	52.15
14	Do[f]	...do	6 50	46.06	11.28	6.20	36.46	131.0	90.67	7,985.0	9,334	6.682	7.370	54.24
15	Betts'	Lump and slack	4 00	53.17	8.73	4.06	34.04	75.8	93.32	4,811.0	5,019	4.426	4.743	51.10
16	Do	...do	7 00					289.0	88.36	8,762.0	10,392	4.453	5.040	52.40

| 17 | Cebu, Comansi | Lump | 5 | 30 | 15.89 | 8.35 | 1.91 | 73.85 | 21.0 | 98.29 | 6,236.5 | 7,347 | 5.985 | 6.089 | 52.89 |
| 18 | Do | do | 7 | 30 | 19.76 | 9.45 | 2.38 | 68.41 | 35.6 | 97.73 | 7,671.5 | 9,041 | 5.775 | 5.907 | |

a The steam pressure and the temperature of the feed water must be considered. The total heat in calories from water at 0° C. of the saturated steam at 7.416 kilograms per square centimeter (105.5 pounds per square inches) is 658.9 and that of the feed water is 28. These together with the kilograms of water, 8,961.5, fed to the boiler, give the equivalent from and at 100° C. at atmospheric pressure as $\frac{658.9-28}{586.5}$ (factor of evaporation) $\times$ 8,961.5 = 10,638 kilograms, 586.5 calories being taken as the latent heat of steam. For convenience, these numbers are taken from Peabody's Tables of the Properties of Saturated Steam, which are generally accepted by engineers. They may be calculated from the following formulæ on which the greater part of all tables is based.

$\lambda = 606.5 + 0.305t$ [v. Regnault, Mém. de L'Acad. (1847), 21, 635].

$\lambda = 589.5 + 0.7028t - 0.00819474t^2 + 0.0000084474t^3$ [Winkelmann, A., Wied. Ann. (1880), 9, 208, 358].

$r = 589.5 - 0.2972t - 0.003214t^2 + 0.0000081474t^3$ (Winkelmann) where λ = the total heat of saturated steam through which the liquid at 0° is changed into steam at any temperature t° and where r = the latent heat of saturated steam, through which the liquid at any temperature t° is changed into steam at t°.

b Calculated from the composition of the ash and the clinker, the calorific value of pure carbon, and the fuel ration and the calorific value of the coal.

c This is the laboratory fuel furnished by the Bureau of Supply. It is "double-screened and picked twice." It was purchased on Circular Proposal No. 248, at a contract price, delivered in Manila, and piled in the coal sheds and yards of the Civil Government at 10.75 pesos (5.375 dollars) per ton of 2,240 pounds.

d This test shows the personal variation in firemen. A man was put on, he could not keep his fire regular and the result was a somewhat low evaporation and at times high chimney temperature and low steam pressure.

e This coal does not represent the vein, for it had evidently lain in the tunnel where it had become water-soaked and considerably silted over. The ash content and clinker-forming ability are therefore high as compared with the run of this coal. It was very difficult to obtain an accurate laboratory sample. The ash shown by the chemical analysis is considerably less than that of the coal actually fired.

f In the use of this fuel, the coal on the grate was not disturbed from start to finish. It was alternately semicoked and spread-fired, and the result is more complete combustion, lower chimney temperature, and greater evaporation.

The loss of heat in the use of the Philippine coal was for the greater part through the smokestack, although a certain amount was due to fine coal falling through the grate; the amount of the latter may be seen from Table IV and of the former from the last column of Table IV and from Table V.

TABLE V.—*Flue temperatures when various coals were burned.*

(Figures give degrees centigrade.)

Source.	West-wald-send, Australia.	Lichzow Valley, Australia.	Karatsu, Japan.	Yubari, Japan.	Labuan, Borneo.	Laguan, Batan Island.	East Batan Island.	Comansi, Cebu
Average	362	395	333	395	388	373	423	366
Maximum	450	517	385	460	510	470	540	195
Minimum	320	320	285	335	280	282	365	315

The above results on Philippine coal are compared in Table VI with the ordinary Australian Coal Numbers 1 and 2, purchased by the Bureau of Supply on Circular Proposal Number 248, and used as a fuel by the Bureau of Science. This coal is *"double-screened and picked twice."* The contract price delivered at Manila, piled in the coal sheds and yards of the Civil Government, is 10.75 pesos (5.375 dollars) per ton of 2,240 pounds. The price at the present time remains practically unchanged.

TABLE VI.—*Calorimeter and steaming tests of Philippine compared with Australian coal Nos. 1 and 2, Table IV as unity.*

(Figures give average percentages.)

	From Table IV.					From Table I.					
	Westwaldsend, Australia.	Lignan, Batan Island. Tests 10-12.	Lignan, Batan Island. Tests 13-14.	East Batan Island.	Comansi, Cebu.	Polillo.	Bulalacao, Mindoro.	Comansi, Cebu.	Camujamayan Valley, Cebu.	Compostela, Cebu.	Sibuguey Bay, Mindanao.
Calorimeter calories	100	94	99	70	94	101	75	94	77	97	102
Actual steaming value	100	64	93	63	84						
Expected efficiency realized	100	68	94	90	90						

Tables IV and V show that the better grades of Philippine coals, Compostela and Comansi in Cebu, western Batan Island, Polillo, etc., can stand on their own merits and successfully be used under stationary boilers and for similar purposes.[5] Coals

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[5] The Bureau of Science has made no experiment to determine their value where forced draft is employed.

of the grade of that from southeastern Batan Island, Dinagat, and Bulalacao in Mindoro, are unquestionably valuable fuel for local consumption. However, it is difficult to transport them and they can hardly be considered satisfactory steaming coals, although I believe they can be used without trouble if the furnaces, grates, and boilers are especially and properly designed and constructed to insure more complete combustion of the coal and more perfect abstraction of the heat from the hot gases. In fact, any Philippine coal will give a greater efficiency if a style of furnace different from any now in use in the Philippines is employed. The fire box of an ordinary furnace should be greatly lengthened, or some device planned for returning the unburned gases through the furnaces before passing up the chimney, in order most satisfactorily to use Philippine coal, or else a considerable portion of the fuel value of the volatile combustible matter, which usually approaches 50 per cent, will be lost. I have often urged [6] the necessity of a setting with an elongated fire box and combustion chamber for burning this class of coal. The combustion space must be long and large enough for the combustible gases and air to mix thoroughly and to produce complete combustion. The United States Geological Survey has expressed the same opinion and further lays especial emphasis on the necessity of an additional baffle wall.[7] Such a wall would undoubtedly cause more perfect mixing and, therefore, more perfect combustion, which is the end desired. It is probable that eddies, such as it is desirable to attain in a reverberatory furnace, caused by any obstacle in the path of the gases, will greatly aid the mixing. Any scheme, which works in the direction of retarding the exit of the gases of the flame stream or of returning the unburned gases through the furnaces before passing up the chimney until combustion of the volatile, combustible matter is completed in the combustion chamber, contains the possibility of greatly increasing the efficiency of Philippine coals. Satisfactory baffle walls would probably be of as much value as a considerable increase in the length of the fire box. A boiler with the same setting as those at the Bureau of Science, but arranged with different baffling forming a tile-roof furnace, has been used on Illinois coals and is said to run at capacities of from 50 to 100 per cent without smoke.

[6] Cox, A. J., *This Journal* (1906), 1, 877; *Sec. A* (1907), 2, 41.
[7] *Bull. U. S. Geol. Surv.* (1907), 325, 62.

It is a difficult task, not yet accomplished, to construct a grate that is suitable under any and all conditions of operation. Various grates, other than the ordinary bar, have been suggested and tried on coals of the subbituminous variety to prevent the loss of fine coal. I have tried a perforated grate without complete success. Mr. A. U. Betts has tried a herring-bone grate which he reports to be very successful. The advantage of a grate of this type over the ordinary gridiron is that shorter, thinner, and more bars may be used without danger of their softening and bending, and in this way the air spaces are increased in number, but diminished in size, without changing the ratio between air space and grate surface. It has been suggested, also, that the loss of combustible matter in the ash could be prevented by burning these coals on a rocking grate. It is hoped that the study of the behavior of Philippine coal and coals of this class will soon result in the discovery of a more satisfactory grate and a method of combustion that will be more economical of coal.

Those Philippine coals which are not wholly satisfactory *a priori* as steaming coals are generally reported to burn exceedingly well when mixed with a certain proportion of Australian coal. I have tried this process with coal from Alcala, Cagayan, which analyzed as follows:

Constituent.	Per cent.
Water	19.3
Volatile combustible matter	38.8
Fixed carbon	30.3
Ash	11.6
	100.0
Calorific value in calories	4,275

While the quantity available was not sufficient to enable me to record any accurate data, the results were satisfactory and I believe the full fuel value of the coal was obtained. Within the last few months, the Bureau of Science has tested 20 tons of coal from the eastern end of Batan Island. The coal was received during heavy rains and was very wet. Its analysis was as follows:

Constituent.	Per cent.
Moisture	21.7
Volatile combustible matter	34.9
Fixed carbon	37.4
Ash	6.0
	100.0
Calorific value in calories	4,609

We tried to operate continuously on this coal alone, but found it was not practicable, as results were obtained similar to those reported in Table IV, and we could not keep up steam.[8]

By mixing with an equal weight of Australian coal we obtained very satisfactory results. The calorific value as shown by the above analysis is equal to 70 per cent of that of the Australian coal used, while the average evaporation for it alone was but 60 per cent of that for Australian coal. The evaporation for three consecutive trials, in which a ratio of 1:1 between Australian and Batan coal was maintained, was slightly more than 70 per cent, which is the theoretical value for the coal. It may be true that the Australian coal itself burns slightly more economically by being thus mixed.

Certain Japanese coals give entire satisfaction when fired under our boilers; Batan coal mixes well with these and gives results as satisfactory as with Australian coal. Other Japanese coals have so fusible an ash that, with the rapid combustion and consequent high furnace temperature continuously maintained under boilers operated at full or over-load, it fuses and eventually closes the air spaces in the grate. This entails a certain amount of labor in keeping the grate free, with a consequent loss of heat during the working of the fires. For this reason the coal in question can be used satisfactorily only under boilers operated at a light load. I made an unsuccessful attempt to find a mixture of one of these coals with that from Batan, which we could operate with the usual grate surface. Light firing would not generate sufficient steam, and heavy firing of any one of the mixtures caused it to cake so badly that it became inefficient. With sufficient grate surface the Japanese coals with fusible ash, mixed in any proportion with that from Batan Island, burned satisfactorily with an average reduction of over 10 per cent of combustible matter in the ash of the Batan coal and a proportional increased evaporation such as was to be expected from the greater calorific value of the foreign coal, but no more grate is needed to burn Batan coal alone. From the standpoint of heat value, the only gain by mixing a small percentage of this class of Japanese coal with that from Batan Island is the reduction of the percentage of combustible matter

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[8] We have since doubled the grate surface, that is, used two boilers where one was sufficient with Australian coal, and find that under these conditions Batan Island coal is satisfactory. With an under-load a boiler can be operated efficiently on this fuel for long periods with the production of practically no smoke.

in the ash, but this saving would hardly be a compensation for the cost of mixing.

From the above it is evident that purchasers of coal under contracts based on the heating value should first give due care to many other conditions which effect the choice of a grade of coal, such as: The kind of equipment, namely, whether the furnaces and other equipment of the boiler setting in which the coal is to be consumed are adapted to the kind of coal under consideration; the friability and fineness of division of the coal; the labor conditions, by which is meant the amount of weight that it is necessary to handle in order to get a unit of heat; and last, but not least, the amount of ash and its fusibility, for these factors have a large influence on the behavior of the coal in the furnaces. Having once decided on the kind of coal that it is desired to purchase, I believe that the delivery of and payment for the coal could be made advantageously entirely on an efficiency basis.

Granting the usefulness of Philippine coal for steaming purposes, there are other points to consider, namely, the economy and the preservation of the supply. In developing, opening up, and working the mines, there is always a large amount of outcrop coal and slack that is unsuited for steaming purposes and which for sake of economy should be used. Experiments with a producer-gas plant[9] have shown that it is possible to use lignites and other poor coals in a gas producer to develop gas for a gas engine, and that the gas from the poor coals has as high a calorific value as that from any other coal which was used. Even when coals burn satisfactorily under a boiler, the process is wasteful as compared with their consumption in a producer-gas plant for the generation of gas-engine power.

Mr. M. R. Campbell,[10] a member of the committee in charge of the producer experiments and of the coal-testing plant, says: "In every case the power produced by one pound of coal in the producer is many times the power produced by the same amount of coal in the steam plant. The ratios of these results run from 1.96 to 3.34; that is, the very best West Virginia coal yielded practically three and one-third times the amount of power when used in the producer that it did in the steam plant, the very poorest coal yielding in the producer practically double the amount of power that it did in the steam plant."

Dr. A. J. Holmes, another member of the committee, says: "We were careful in any of this work, where we would get the boiler test, to find out how many pounds of coal were necessary to develop a horsepower per hour, and found that when we put that same coal through the gas producer

[9] *Prof. Papers U. S. Geol. Surv.* (1906), No. 48, pt. 3.
[10] *Econom. Geol.* (1907), 2, 287.

it would require generally less than half the amount of coal in pounds to develop a horsepower that it required in the steam boiler. We worked through a series of averages, using nearly 150 tests made in that way, and, comparing the results obtained from the same coals in the gas producer and under the boiler, got on an average about 2.6 times as much power from every ton of coal in the gas producer as we did under the boiler."

It is important in firing coal under stationary boilers to note that Philippine coals are noncoking, do not swell, burn steadily, do not clinker, have very little ash, are easily fired, and do not soot the boiler tubes to any such extent as does Japanese, Australian, or Bornean coal, and especially is it important to note that with these physical properties they would be ideal to handle in producer-gas plants. The Bureau of Science has been negotiating for a long time with manufacturers of gas producers, and I am pleased to report that coal from the southeastern end of Batan Island has been successfully used in a German gas producer and that the Bureau of Science has ordered a 67-horsepower Otto producer unit, with the corresponding engine and electric generator, direct coupled, to be used as one unit of our plant which supplies power for the Philippine General Hospital, the Philippine Medical School, and the Bureau of Science. It is expected that this unit will be installed and in readiness for experimentation with the local coals within the year 1912. For the production of power the utilization of our low-grade and outcrop coal for producer gas seems extremely promising. It is anticipated that such a plant as we shall install, when using the poorest Philippine coal, can compete with the best steam plant in the Islands and, especially, that it can burn successfully the slack and waste products which are not utilizable for steam purposes. It is probable that the poorest coals employed in a producer-gas plant may become as available as the best grades of coal used in a steam plant or, perhaps, even succeed the steam plant altogether for stationary work.

THE ALCOHOL INDUSTRY OF THE PHILIPPINE ISLANDS. PART II.[1]

DISTILLED LIQUORS; THEIR CONSUMPTION AND MANUFACTURE.

By H. D. GIBBS [2] AND W. C. HOLMES.

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

CONTENTS.

INTRODUCTION.

From earliest times, the natives of the Philippine Islands have been, to a certain extent, addicted to the use of intoxicating beverages, and, throughout the Spanish history of the Archipelago, references to its baneful influences and to measures to restrict the evil are continually to be found.

Antonio Pigafetta [2] first records that at the Island of Mazava, the second of the Philippine group sighted by Europeans, at which Magalhaes anchored on March 28, 1521, the native kings got so drunk that they could not harvest their rice crop.

"The kings replied *(to Magalhaes)* that every hour he wished the pilots were at his command, but that night the first king changed his mind, and

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[1] Part I. A study of some palms of commercial importance, with special reference to the saps and their uses, by H. D. Gibbs *et al.*, was published in *This Journal, Sec. A* (1911), 6, 99 to 206.

[2] Associate professor of chemistry, University of the Philippines.

[2] Blair and Robertson, The Philippine Islands. Cleveland, Ohio (1906), 33, 129.

in the morning when we were about to depart, sent word to the captain-general, asking him for love of him to wait two days until he should have his rice harvested, and other trifles attended to. He asked the captain-general to send him some men to help him, so that it might be done sooner, and said that he intended to act as our pilot himself. The captain sent him some men, but the kings ate and drank so much that they slept all the day. Some said to excuse them that they were slightly sick."

In 1565, Governor Legaspi recognized the evil effects of the native beverages. He ordered: [3] " 'that wine should not be brought or sold within the camp, and that the Spaniards should not buy it. He told Tupas and the chiefs that, as the Spaniards were not accustomed to this land, and were but recently come thither, it was not good for them to drink this wine, and that some of them had become sick. And he asked that Tupas neither consent to it, nor bring wine to the Spaniards.' The traffic still went on nevertheless, 'secretly and at night,' and the Spaniards gave themselves up to it entirely, saying 'that it was better than that of Castilla.' "

In a document which purports to be a letter [4] from Mirandaola to the king, dated June 8, 1574, it is stated that the natives "have wines of many kinds: brandy, made from palm-wine (which is obtained from the cocoa-nut palm, and from the wild nipa palm); *pitarrillos*, which are the wines made from rice, millet, and borona; and other wines, made from sugar-cane."

Captain Artieda [5] wrote:

"The cocoa-palm offers the greatest means of sustenance to the natives, for they obtain from it wine, fruit, oil, and vinegar. * * * The natives sustain life by eating little and drinking much—so heavily, that it is a marvel if they are not drunken all the time, or at least from noon on. And the more important their position, the more intoxicated do they become, for they have more to spend for this purpose."

In 1619, Captain Sebastian de Pineda [6] wrote to the king regarding a great evil which, if not checked, will in time cause great evil to the country. (Mexico.)

"This consists in the fact that there are in Nueva España so many of those Indians who come from the Filipinas Islands who have engaged in making palm wine along the other seacoast, that of the South Sea, and which they make with stills, as in Filipinas, that it will in time become a part reason for the natives of Nueva España, who now use the wine that comes from Castilla, to drink none except what the Filipinos make."

In 1762, Governor Anda [7] ordered the governor of Guagua to forbid the sale of nipa wine and destroy all found in the taverns.

In 1837, Blanco [8] writes of the injurious effects of the coco distillates as follows:

"If after the fermentation of the tuba, the liquor is distilled over, an alcohol, more or less passable is obtained. This beverage is good for the natives and Europeans who are accustomed to it, but the drinkers who are

[3] *Ibid.* 2, 137.
[4] *Ibid.* 3, 55, 56 foot-note.
[5] *Ibid.* 3, 202.
[6] *Ibid.* 18, 184.
[7] *Ibid.* 49, 148.
[8] **Flora de Filipinas,** 1st ed. (1837), 719; 2nd ed. (1845), 497.

not accustomed to it find in the liquor a disagreeable odor and taste. After a time it causes terrible harm to them, producing premature old age, disorders of their physic, loss of appetite, sleeplessness, dropsy, boils, vomiting, loss of intellectual faculty and they become stupid, are seized with trembling, show lack of memory and finally insanity results. These shameful sicknesses are also caused by European wine and alcohol although more slowly."

Monopolies of the distilled spirits industries were common under the Spanish rule. It is reported [9] that, "Such spirits as were distilled in this country from the coco and nipa palms were monopolized in 1712 by Don Martin de Urzua, Governor of these islands, upon request of the municipal council, by reason of the abuse which the natives made of the same, being then farmed out for the sum of 10,000 [10] pesos. In 1714 and 1720, royal orders were received wherein it was provided that under no pretext should manufacture or sale of alcohol, made from the sugar cane, be permitted or consented to. * * * Later on, by royal order dated 1725, the monopoly was abolished, and the municipal council again prayed for it as a punishment for drunkenness." * * *

"In 1862 the alcohol monopoly was finally done away with, and two years later the trade and manufacture of all kinds of alcohol was declared free."

Jagor,[11] who traveled in the Philippines in 1859–60, states concerning the traffic under the Spanish rule in liquors distilled from sugar—containing saps, and molasses:

"The proceeds of this monopoly (wines and liquors) were rated at 1,622,810 dollars in the colonial budget for 1861; but its collection was so difficult, and so disproportionately expensive, that it nearly swallowed up the whole profit. It caused espionage, robberies of all sorts, embezzlement, and bribery on a large scale. The retail of the brandy by officials, who are paid by a percentage on the consumption, did a good deal to injure the popular respect for the government. Moreover, the imposition of this improper tax on the most important industry of the country, not only crippled the free trade in palms, but also the manufacture of raw sugar; for the government, to favor their own monopoly, had forbidden the sugar manufacturers to make rum from their molasses, which became in consequence so valueless, that in Manila they were given to the horses. The complaints of the manufacturers at last stirred up the administration to allow the manufacture of rum; but the palm-brandy monopoly remained intact. The Indians now drank nothing but rum, so at last, in self-defense, the government entirely abandoned the monopoly (January, 1864). Since that, the rum manufacturers pay taxes according to the amount of their sales, but not upon the amount of their raw produce. * * * The practice of drinking brandy has naturally much increased; it is, however, a very old habit."

[9] *Rep. Coll. Int. Rev., Rep. Phil. Comm.* (1905), pt. 4, 187. Editorial from *El Mercantil.*

[10] We have been unable to find the references to the particular document relating to this case. James A. Robertson of the Philippines Library, whose aid was solicited, writes: "I do not find this specific instance, but there are many others in the history of the Philippine Islands, most of them for more than this amount and all annually."

[11] Travels in the Philippines. London (1875), 74.

Accounts of the excessive use of alcoholic beverages, made from rice and palm saps by the natives of Borneo, are given by Henry Ling Roth,[12] and various other authors speak of parallel conditions existing upon other islands and portions of tropical Asia.

There is a firmly settled opinion in the minds of a number of persons who have come in contact with the question and who are in a position to know, that the prevalence of the drinking of *tuba*, a term for fermented but not distilled palm saps, is much more serious, at the present time, than the drinking of distilled beverages.

The Attorney-General of the Islands, in a special report, dated July, 1909, states:

"Two-thirds of the fiscals of the Archipelago declare that local drinks, such as tuba, coconut and nipa wines and basi are mainly responsible for the crimes against persons, chiefly those of assault and battery, and homicide. During the hot and dry season a positive increase in these crimes is more noticeable in several provinces or districts. Their number is, however, greater in the Visayan Islands than in Luzon, and in the Islands of Antique and Cebu intoxication produces such a peculiar frenzy that the drinker becomes irresponsible."

Detailed statements from a number of provinces are included and the report from Capiz is quoted, for the reason that it is somewhat typical of the nipa districts where little or no commercial use is made of the vast resources of the nipa areas. The quotation is as follows:

"The crimes most frequently committed in the jurisdiction of this court are those of homicide, murder, and assault and battery. These crimes are generally committed from April to December.

"The causes of the commission of these crimes are, in the first place, intoxication, for this province abounds with tuba; it costs almost nothing, and many people of the interior towns live in the nipales, so that they have tuba within their reach at all hours of the day. The owners of said nipa plantations, since wine distilleries have been closed, pay little attention to their plantations and leave them to the care of their watchmen or *encargados*, who with other persons avail themselves of the tuba without or occasionally with the knowledge, of the owners.

"In the second place, the habit of the poor people of the interior towns of carrying a bolo at the waist from morning till night, and even when intoxicated, results in the frequent use of this weapon even in the most trivial differences. So it is that many of the crimes of homicide and assault and battery committed in this province are due only to insignificant questions or resentments, and at times the cause is not even known. In the third place, there is the lack of instruction of those living outside of the towns, or in the mountains, in the principles of justice. They want to settle their quarrels by means of the bolo, not knowing any different form of adjusting their controversies; they do not know how to resort to the courts of justice to settle their grievances."

The Internal Revenue Agent[13] of Nueva Caceres states: "My personal

[12] The Natives of Sarawak and British North Borneo. London (1896), 1, 391.
[13] Special report, February 15, 1911.

observations lead me to believe that 'tuba fiends' are, next to morphine fiends, the most degenerate specimens of humanity I have ever seen."

These are a few of the statements made by various persons and from reports to be found upon the question, and many more could be quoted. It seems to us that the most reasonable conclusion to be deduced from the evidence is that drinking of undistilled beverages is carried to excess in some parts of the Islands, distilled beverages in others, and again there are localities where excesses are to be encountered only on rare occasions.

In some parts of the Islands not only feast days and holidays are largely given over to drinking, but a certain proportion of the natives in their regular routine demand a certain amount of alcoholic stimulant. Such a person likes to fortify himself with a glass of *vino* before following the carabao drawing the primitive plow through the mud of the paddy, and later while working at the harvest and while engaged in the laborious work of hemp stripping. In some localities large quantities of distilled spirits are consumed regularly with an extra allowance on holidays and during fiestas. The reader must not gain the impression that a general condition of excessive drinking prevails throughout the Islands, for this is not the case. Some allowance, we believe, must be made for the exaggeration of travelers, whose observations have been somewhat superficial and restricted. The per capita consumption of distilled liquors is very small; for 1910, 1.36 liters, and for 1911, 1.32, but in some localities the indulgence is excessive and the effects are evil. The consumption is constantly increasing.[14] No estimates can be made of the quantities of fermented but not distilled beverages manufactured and consumed.

The production of alcohol since the enactment of the present internal revenue law to the end of the fiscal year 1910 was given in Part I, Table III, of this article. The data for the past year, which have just been made available, can be found in the Seventh Annual Report of the Collector of Internal Revenue. They show very little change from 1910, except that the amount of denatured

[14] The Collector of Internal Revenue states, Seventh Annual Report (1911), 10: "The total output from the registered distilleries during the year was 10,471,299 proof liters, about 1 per cent less than during the fiscal year 1910, and about 9 per cent more than during the fiscal year 1909. The decrease, as compared with the fiscal year 1910 output, is due to the abnormal removals from distilleries in anticipation of the increase in the tax rate which became effective during the fiscal year 1910." Figures so far available for 1912 show that the industry is undergoing a healthy increase.

alcohol consumed has more than doubled. None of the preceding statistics are now applicable to the non-Christian tribes. These people are not allowed to traffic in distilled beverages, but are restricted to their own drinks, which are mostly made of fermented rice.[15] No distilleries are located in their country.

The greater proportion of the alcohol distilled in the provinces, especially that produced from the sap of the nipa palm, is shipped to Manila where it is again rectified and manufactured into a considerable number of different beverages, the majority of which are imitations of various imported and well-known articles.

The natives in this way consume 98.8 per cent of the rectified alcohol produced. The other 1.2 per cent is partly exported and partly used for industrial purposes. At the present time the distillers and rectifiers of Manila are putting about 22 beverages on the market, as follows:

TABLE I.—*Beverages made in the city of Manila from distilled spirits and their average alcoholic strength.*

Kind.	Average proof.	Kind.	Average proof.
Anisado	70	Elixir	78
Anis	78	Gin	80
Anisette	78	Ponche Venus	63
Blackberry brandy	25	Jerez	25
Benedictine	60	Mallorca	70
Carabanchel	75	Moscatel	28
Cognac	78	Maraschino	40
Crème de coco	67	Rhum	78
Crème de café	71	Vermouth	28
Crème de menthe	60	Vino de nipa	70
Chartreuse	61	Whisky	78

The labeling of the majority of these beverages is in imitation of well known brands and in many cases is in violation of the Food and Drugs Act (number 1655 of the Philippine Commission, May 18, 1907). A few examples are: Scotch Whisky, Non Plus Ultra Whisky, Cognac, Champagne Cognac, Cognac Fine Champagne, Very Old Cognac, 3 Star Cognac, Best Special Brandy, Gin, Rotterdam Gin, Holland Gin, Irish Gin, Pineapple Gin, Honest Gin, Love Gin, Jamaica Rum, Creole Rum, Sultana Rum, Florida Water, Church Wine, Consecration Wine, Moscatel for Consecration, Sherry, Butterfly Sherry, Sherry Algeciras, Tinto Seco, and Tinto Dulce.

[15] An account of various fermented but not distilled beverages will be given in Part III of this article, which is now in preparation.

The most popular and most widely consumed beverages are the artificially flavored gin and *anisado* [16] and the untreated distillates *vino de nipa* and *vino de coco*.

During the fiscal year [17] 1910, there were collected 35,144.18 pesos tax on imitation wines of domestic manufacture. During the period from August 7, 1909, to June 30, 1910, there were removed for consumption, tax paid 306,149 gauge liters of domestic imitation still wines, containing not more than 14 per cent of alcohol, and 55,082 liters, containing more than 14 per cent of alcohol. The data for the fiscal year 1911 are tabulated as follows:

TABLE II.—*Imitation wines (domestic manufacture). Number of gauge liters removed for domestic consumption during the fiscal year 1911.*

Alcoholic content.	Bulacan.	Manila.	Pampanga.	Total.
14 per cent of alcohol or less (pays 8 centavos per liter)	3,045	453,258.46	------------	456,303.46
25 per cent of alcohol or less (pays 15 centavos per liter)	8,760	68,575.00	1,145	78,480.00
Total	11,805	521,833.46	1,145	584,783.46

Total tax paid, fiscal year 1911, 48,276.28 pesos.

These beverages were manufactured almost entirely from alcohol produced from the nipa palm.

The total production of alcohol from the coconut palm is consumed locally as the beverage *vino de coco*, while that from the nipa palm is partly consumed as the pot still beverage *vino de nipa* and partly rectified and made into other beverages.

CLASSIFICATION OF THE DISTILLERIES AND ANALYSES OF THEIR PRODUCTS.

Samples of the various distillates made from the fermented saps of the nipa and coconut palms and from molasses, representing all the various geographical districts in which distilleries are in operation, were collected by the agents of the Bureau of Internal Revenue for the purpose of investigating the products of the distilled liquor industry. The selections were also made to rep-

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[16] Anisado, anis, anisette, carabanchel, and mallorca are all varieties of the same type of beverage. They are made from alcohol, sugar, water, and oil of anise. When sugar is used in considerable quantity with small amounts of oil of anise, the beverage is called *anisado mallorca* or *mallorca*. Carabanchel is sweeter and contains more flavoring substance.

[17] *Sixth Ann. Rep. Coll. Int. Rev. P. I.* (1910).

resent every class of distillery and distilling apparatus in use. The latter includes nearly every known type, from the usual pot or whisky still to the continuous stills, principally of French manufacture, employed in the provinces of Bulacan, Pampanga, and Manila; however, the great majority of the smaller establishments are equipped with stills of Manila manufacture of the simple pot or whisky type. Several types of stills from the primitive to the most modern are illustrated in plates at the end of this part of the article and also in some of the plates published in Part I.

A few years ago there were in operation in the provinces about 600 primitive distilleries which have entirely disappeared except for purposes of illicit distillation. These were located in Albay, Ambos Camarines, Bataan, Cagayan, Capiz, Ilocos Sur, La Laguna, La Union, Moro, Pangasinán, Palawan, Sámar, Surigao, Tayabas, and Zambales.

The distilling apparatus consisted of a fire place, a pot and condenser in one, and a delivery tube for carrying off the distillate. The fire place was built of stones and mud and was usually without chimney for carrying off the smoke. The pot and condenser was composed of a wooden cylinder between two iron pans. The bottom pan rested on the fire place and the top pan was kept filled with cold water during the distilling operation and thus acted as a condenser. The vapors condensing on the convex under surface of the pan dropped into the delivery pipe of bamboo and were carried to the receiving vessel on the outside. The wooden cylinder composing the side walls of the still was often cut from a single log, and in the apparatus of larger capacity was built like a barrel with rattan hoops. The joints connecting the top and bottom with the metal vessels were made tight with mud, clay, rags, or any convenient material. The larger pots were connected with a lever, by means of which they were swung clear of the lower pan for purposes of cleaning and filling. The capacities varied from about 750 liters down to small portable stills used for illicit distilling, sometimes as small as 20 liters capacity.

A larger apparatus is illustrated in Plate I. Small illicitly operated stills of this type are continually being discovered by the Internal Revenue Agents in out of the way parts of the country.[18]

The distillates produced with this crude apparatus averaged about 25 per cent alcohol and seldom ran over 30 per cent. They were much prized by the natives of some localities and were preferred to gin, anisado, and other beverages of higher proof manufactured in more modern apparatus. This condition still exists in some portions of the Islands, although the tendency of

[18] Further descriptions of primitive distilleries are found in *Rep. Coll. Int. Rev. P. I., Rep. Phil. Comm.* (1905), pt. 4, 163, 189, and 191.

the native taste is toward a stronger beverage, containing in the neighborhood of 40 per cent alcohol.

The Collector of Internal Revenue reports: [19]

"On June 30, 1910, there were in operation throughout the Islands 68 registered stills of modern type, as compared with 78 in operation on the same date of the preceding year, and 68 on the same date in 1908. During the year, 60 illicit stills were captured by internal-revenue agents. * * * All of the illicit stills captured were of the ancient type known as the *caua*, of which there were about 600 in operation throughout the Islands prior to the taking effect of the Internal Revenue Law in 1904. The captured stills were small, with a daily capacity of 10 to 50 proof liters each."

These data are tabulated as follows:

TABLE III.—*Illicit stills captured by officers of the Bureau of Internal Revenue during fiscal years 1910 and 1911 by provinces.*

Provinces.	Fiscal year.		Provinces.	Fiscal year.	
	1910	1911		1910	1911
Albay	17	1	Nueva Vizcaya	1	
Cagayan	6	4	Pangasinan	30	36
La Laguna	4	9	Tayabas	2	1
Moro		1	Total	60	52

TABLE IV.—*Distilleries in operation June, 1911, at the end of the fiscal year.*

Province.	Distilleries.	Province.	Distilleries.
Albay	3	Manila	8
Ambos Camarines	3	Pampanga	5
Bulacan	5	Pangasinan	12
Capiz	2	Samar	1
Ilocos Sur	1	Tayabas	15
La Laguna	12	Total	67

The following classification of distilleries and distilling apparatus has been employed for the purposes of this investigation.

A. A distillery where the methods are cleanly, the immediate surroundings sanitary, and the general business methods of a superior order.

B. The conditions of "A" are modified by being less cleanly, the surroundings not entirely sanitary, and the business methods not of a superior order.

C. The methods are uncleanly, the surroundings unsanitary, and the business methods unsatisfactory.

[19] *Sixth Ann. Rep. Coll. Int. Rev. P. I.* (1910), 10.

D. The ordinary modern *caua* or pot still.   Illustrated in Plate II.

E. The continuous process still.

F. The modern rectifier, distilling crude distilled spirits.   Illustrated in Plates V and VII.

G. The modern rectifier distilling the raw materials directly.

The analytical results are classified in the following tables. With the exception of the figures for density and percentage of alcohol, all are expressed as grams per hundred liters of hundred proof spirits.   The analytical methods employed are those of the Association of Official Agricultural Chemists,[20] with the modifications suggested by one of us.[21]

TABLE V.—*Analyses of distilled liquors, alcohol, and beverages made therefrom.*

VINO DE NIPA.

Laboratory number.	Source.	Distillery.	Apparatus.	Density.	Alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Higher alcohols.	Aldehydes.
					Per ct.						
17	Domalandan, Lingayen, Pangasinan	A	D	0.9557	36.6	36.0	181.0	136.0	180.0	61.7	14.6
18	Poblacion, San Isidro, Pangasinan	C	D	0.9717	25.0	114.0	534.0	462.0	217.0	64.6	11.6
20	Tambac, D a g u p a n, Pangasinan	B	D	0.9670	28.15	50.8	388.0	282.0	219.0	50.6	9.0
49	Bobolusan, L a o a n g, Samar	B	D	0.9658	28.9	66.7	358.0	287.0	270.0	83.0	10.5

NIPA DISTILLATE; CRUDE ALCOHOL.

					Per ct.						
28	Santo Rosario, Hagonoy, Bulacan	B	E	0.9350	49.3	27.8	91.5	77.7	116.0	72.0	5.0
82	Atlog, Malolos, Bulacan.	C	E	0.9124	58.95	11.5	63.6	52.8	116.0	80.5	5.8
35	Calanate, M a l o l o s, Bulacan	B	E	0.9304	51.5	31.0	99.2	63.1	126.0	74.8	11.3
46	Santo Niño, Paombong, Bulacan	A	E	0.9400	45.2	8.4	136.0	111.0	161.0	76.5	10.7
38	Santo Rosario, Hagonoy, Bulacan.	C	E	0.9337	50.15	16.9	107.0	96.6	171.0	81.0	8.4
42	San Esteban, Macabebe, Pampanga	B	E	0.9000	62.45	13.3	49.4	39.4	162.0	55.6	9.9

[20] *U. S. Dept. Agr. Bur. Chem.* (1906), Bull. 107, 98.
[21] Holmes, *This Journal, Sec. A* (1910), 5, 23.

TABLE V.—*Analyses of distilled liquors, alcohol, and beverages made therefrom*—Continued.

NIPA DISTILLATE; RECTIFIED ALCOHOL.

Laboratory number.	Source.	Distillery.	Apparatus.	Density.	Alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Higher alcohols.	Aldehydes.
					Per ct.						
37	Calangayan, Lubao, Pampanga	B	G	0.8165	93.9	4.5	4.2	1.1	103.0	24.4	1.9
43	San Esteban, Macabebe, Pampanga	B	G	0.8400	85.85	4.8	5.2	1.1	127.0	80.0	7.6
47	Santo Niño, Paombong, Bulacan	A	{E}{F}	0.9170	96.4	2.0	1.4	1.1	65.5	17.7	5.0
48	Santo Rosario, Hagonoy, Bulacan	A	G	0.8184	93.9	1.8	16.9	1.1	148.0	18.0	4.0
58	Manila	B	F	0.8164	93.9	1.1	1.7	1.1	226.0	38.1	13.1
66	Manila	C	F	0.8230	94.9	trace	3.6	0.3	7.2	27,9	2.5
69	Manila	A	F	0.8140	94.9	1.2	4.7	0.4	621.0	227.0	22.5

BEVERAGES FROM NIPA DISTILLATES.

Laboratory number.	Source.	Description.	Distillery.	Apparatus.	Density.	Alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Higher alcohols.	Aldehydes.
						P. ct.						
31	Atlog, Malolos, Bulacan.	Carabanchel	C	E	0.9875	21.35	8,654.	48.6	48.6	123.0	155.0	16.0
65	Manila	Tinto seco	C	F	0.9900	16.05	6,842.	......	69.2	34.3	131.0	10.9
59	Manila	Rice wine^a	B	F	1.029	17.75	37,341.	469.0	226.0	88.0	67.2	7.1
44	Santo Niño, Paombong, Bulacan.	Anisado	A	{E}{&}{F}	0.9720	23.9	833.	68.0	22.3	157.0	77.8	12.5
26	Santo Rosario, Hagonoy, Bulacan.	Anisado	B	E	0.9712	25.0	222.	10.3	7.4	113.0	85.9	7.3
8	Pasig, Rizal	Anisado	B	—	0.9770	26.2	3,917.	8.5	2.3	94.9	71.9	7.1
6	Pasig, Rizal	Gin	B	—	0.9668	27.75	162.	6.1	3.2	90.4	34.7	6.3
33	Calnate, Malolos, Bulacan.	Gin	B	E	0.9588	34.7	284.	10.2	8.9	147.0	70.2	6.5

ᵃ Made from nipa.

TABLE V.—*Analyses of distilled liquors, alcohol, and beverages made therefrom*—Continued.

COCO DISTILLATES; VINO DE COCO.

Laboratory number.	Source.	Distillery.	Apparatus.	Density.	Alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Higher alcohols.	Aldehydes.
					Per ct.						
22	Iriga, Camarines.........	A	E	0.9640	30.5	20.1	454.0	331.0	241.0	59.6	2.7
24	Nagcarlang, La Laguna.	A	D	0.9600	32.0	29.7	463.0	401.0	314.0	77.5	4.1
25	Luisiana, La Laguna.....	B	D	0.9520	36.6	17.5	364.0	286.0	272.0	115.0	8.8
50	Masaranag, Guinoba- tan, Albay	C	D	0.9635	32.75	26.9	419.0	333.0	222.0	52.0	2.7
51	Gapo, Camalig, Albay...	B	D	0.9636	32.75	34.8	379.0	345.0	214.0	77.6	3.5
54	Cotta, Lucena, Tayabas.	B	D	0.9410	45.2	21.2	282.0	262.0	378.0	65.3	7.1
55	Salinas, Lucena, Taya- bas	C	E	0.9340	49.3	18.7	274.0	263.0	442.0	116.0	24.6
56	Galangulang, Lucena, Tayabas	A	D	0.9416	45.2	22.8	218.0	190.0	347.0	48.9	3.3
64	Manila..................	C	F	0.9637	32.75	65.0	132.0	124.0	79.7	45.0	3.2
bX	Illicit Vino de Coco......				40.9	81.2	127.0	117.0	150.0	38.2	4.5

b X was a sample of illicit *bino* seized in La Laguna Province on February 7, 1911, and furnished by Internal Revenue Agent Patstone. It was made in a small sheet metal still of a simple form.

Illicit *vino de coco* is often given an additional flavor and aroma by conducting the condensing vapors through leaves of the banana and other plants, and the product is said to be generally preferred by consumers.

DISTILLATES FROM MOLASSES.

Laboratory number.	Source.	Description.	Distillery.	Apparatus.	Density.	Alcohol.	Total solids.	Total acids.	Volatile acids.	Esters.	Higher alcohols.	Aldehydes.
						P. ct.						
1	Gerona, Tarlac	Anisado	C	F	0.9754	22.45	151.0	110.0	92.9	76.4	79.2	13.2
4	Paniqui, Tarlac....	Alcohol......	B	E	0.9327	45.30	25.0	64.1	57.9	49.5	53.3	8.5
13	Paoad, Santa, Ilo- cos Sur.	Vino de ca- fé.	B	G	0.9570	36.60	400.0	16.6	9.5	8.4	81.5	10.8
15	Paoad, Santa, Ilo- cos Sur.	Alcohol......	B	G	0.8392	81.65	1.8	8.2	4.5	13.5	106.0	9.8

The average data for pot still *vino de coco*, pot still *vino de nipa*, crude alcohol of nipa origin, and rectified alcohol made from nipa in rectifying stills, are given in Table VI. In several instances values obviously abnormal are omitted from consideration.

TABLE VI.—*Average composition of the various distillates.*

Class of liquor.	Total solids.	Total acids.	Volatile acids.	Esters.	Higher alcohols.	Alde- hydes.
Vino de coco	24.0	356.0	301.0	304.0	76.5	4.4
Vino de nipa	66.9	364.0	291.0	221.0	65.0	11.4
Crude alcohol	18.1	91.0	73.4	142.0	73.3	8.5
Rectified alcohol	2.2	8.5	0.9	90.0	34.3	4.2

It will be seen that the nipa and coconut distillates are similar in character, although in general those from the nipa palm sap run comparatively lower in esters and higher in aldehydes than the others. The influence of the type of still on the composition of the liquor is clearly indicated by a comparison of the *vino*, crude and rectified alcohols of nipa origin. It is surprising that the elimination of the secondary distillation products and especially of esters in the rectifying stills is not more thorough. In general, the most significant characteristic of liquors distilled from palm saps is their remarkably high content of secondary distillation products and notably of acids and esters.

It has been stated that the greater proportion of alcohol distilled in the provinces from fermented nipa sap and sugar molasses is shipped to Manila where it undergoes a certain amount of rectification and is manufactured into a considerable number of products, and this statement may be illustrated by a description of the manufacture of a local rum. After a double distillation in a still of a rather simple type, the liquor has the following composition (quantities except alcohol expressed as grams per 100 liters) :

Alcohol	61.84 per cent.
Total solids	Negligible.
Total acids	5.6
Esters	55.4
Higher alcohols	58.3
Aldehydes	8.6

After dilution and the addition of flavoring and coloring matter, the "rum" has the following composition:

Alcohol	36.6 per cent.
Total solids	3,071.0
Acidity	18.4
Esters	116.6
Aldehydes	11.1

The total solids are of a saccharine nature, and the coloring material is caramel.

The manufacture of gin is of considerable importance, and

some 14 samples of gins of local origin have been analysed in the past three years. The average of these analyses may be compared in the following table with the average results of the analyses of seven samples of Holland and six of English gins obtained through the Bureau of Customs.

TABLE VII.—*Analyses of gins.*

Kind.	Density.	Alcohol.	Acids.	Esters.	Higher alcohols.	Aldehydes.
		Per cent.				
Native	0.950	40.9	7.0	52.5	59.1	3.1
Holland	0.943	47.0	5.7	22.3	56.2	2.9
English	0.944	49.9	1.3	10.6	30.0	3.5

There is a distinct variation between these different gins corresponding to a variation in the degree of rectification which the liquors have undergone. As a rule English gin is made from highly rectified spirits, while in Holland and more particularly in the Philippines the secondary distillation products are less thoroughly removed. However, it should be stated that several brands of Philippine gin could not be easily distinguished, by chemical analysis, from the best English gin. The only distinctive characteristic of Philippine gin in general would seem to be a comparatively high ester content, as would be expected from the foregoing analyses of rectified nipa distillates. Although the total number of samples examined is not large, it is believed that these generalizations are justifiable.

Considerable quantities of "essences" or flavoring materials are imported into Manila for the manufacture of distilled beverages. A peculiar so-called "gin oil" has been discovered in use by one of the distillers. This consists of 4 per cent of ethyl alcohol, 92 per cent of amyl alcohol and 4 per cent of oil of juniper. The Food and Drug Board has taken cognizance of the question, and will endeavor to improve the quality of the gins of local manufacture.

THE DISTILLATION OF VINO DE COCO.

From the analyses of the considerable number of distilled liquors of Philippine origin recorded in Tables V and VI, it is seen that the most significant characteristic of these liquors in general and of *vino de coco* and *vino de nipa* in particular is their remarkably high content of secondary distillation products and especially of acids and esters. The principal object of the work herein described was to obtain a more particular knowledge of the distillation of *vino de coco* in the hope that improvements

in the methods of distillation might be suggested. Any conclusions arrived at from the study of *vino de coco* are equally applicable to *vino de nipa* distilled from the pot still. It had been intended at the same time to carry out, along practical lines, a study of the fermentation of coconut sap, and a number of samples were collected with this end in view, but the difficulty encountered in inhibiting fermentation changes in these samples during transportation to the laboratory in Manila was not completely overcome, and this important phase of the question was left for future investigation under more favorable conditions. It is an important question, and should not be neglected.

The first distillery visited was at Nagcarlan, La Laguna Province, where with the assistance of Internal Revenue Agent Patstone a distillation was supervised on April 7, 1911, and samples obtained for analysis as hereinafter described.

The still employed was a modern pot still, provided with a small doubler and heated by direct flame. (Plate II.) After each distillation, the residue in the still, termed *tabad* (Tagalog), is drawn off as completely as possible, leaving about 57 liters of liquid, which, owing to the manner of construction of the still, can not be withdrawn. To this are added some 1,200 liters of fermented coconut sap and about 20 liters of *bating* and *parasan* (Tagalog) which correspond to the "heads" and "tails" rejected from the previous run. After the still is started, a trap, placed on the delivery tube beyond the condensing worm, is left open until the still runs true, that is, until the weak alcohol left in the condenser from the previous run has been discharged. Then 2 liters of the first distillate, called *bating* (Tagalog), are drawn off. The heads and former distillate are considered a poor beverage, and are returned to the next charge for redistillation. The trap is then closed and the distillate proper called *banto* (Tagalog), amounting to about 200 to 250 liters, is run into the storage tanks. Finally from 15 to 20 liters of tails or weak alcohol are collected separately and later returned to the next run. Two distillations a day are made whenever the *tuba* is available.

The gauge liters obtained are calculated from the rise in level of the distillate in the storage tank into which it is run. To obtain the proof liters, the trap is regulated so that the distillate is slowly dropping throughout the run, giving a composite sample which is used for a hydrometer reading. The transition point between the beverage and the tails is found by an attendant who is sufficiently experienced to judge of the alcoholic content of the distillate from its taste. These methods for the determination of gauge and proof liters are less accurate than those which will later be described as employed at a second distillery.

In the distillation supervised by us, the still contained 1,216 liters of fermented coco sap, 57 liters of residue in the still from the previous charge, 19 liters of tails, and 2 liters of heads, making a total of 1,294 liters. A sample of the charge was taken for analysis, but, inasmuch as we have reason to believe that the salts of mercury added as a preservative did not com-

pletely inhibit all fermentation changes, the analysis of this sample is not given.

During the distillation, 10 samples were taken for analysis. Of these, 1 was from the heads, 8 from the beverage the total volume of which was 231 liters, and 1 from the tails. The analyses are given in Table VIII. All figures except for alcohol are given as grams per one hundred liters, and that notation is to be understood to apply in all of the following analyses except where otherwise specified. The alcohol is reported in percentage by volume.

TABLE VIII.—*Distillation of vino de coco at Nagcarlan. Analyses of the various fractions collected during a still run.*

Sample number.	Discription.	Liters in fraction.	Alcohol.	Acids.	Esters.	Higher alcohols.	Aldehydes.
			Per cent.				
2	Heads	2	51.82	96.6	2,923	1,541.0	21.2
3	Beverage fraction 1	1	61.40	130.0	3,276	1,517.0	27.2
4	Beverage fraction 2	5	62.76	140.4	2,653	1,397.0	26.0
5	Beverage fraction 3	5	59.89	162.5	1,516	855.0	18.4
6	Beverage fraction 4	10	58.14	156.0	944	232.0	14.2
7	Beverage fraction 5	50	53.72	152.0	291	76.4	6.4
8	Beverage fraction 6	50	42.95	187.2	111	48.8	5.1
9	Beverage fraction 7	50	29.67	250.3	113	35.3	2.4
10	Beverage fraction 8	60	17.17	299.0	118	29.6	2.8
11	Tails	17	11.08	310.0	106	12.8	3.9

The residue in the still was found to contain slightly over 0.1 per cent of alcohol and comparatively insignificant amounts of secondary distillation products except that it contained over 0.4 per cent of acids. The analyses of the charge and of the residue have been rejected as being somewhat untrustworthy, inasmuch as samples of fresh *tuba*, preserved in the same way, apparently underwent certain changes.

It is evident that a considerable portion of the higher alcohols, esters, and aldehydes distill over in a comparatively short time, whereas the acids come over in increasing amounts as the distillation is continued.[21]

With these data at hand, it is possible to consider intelligently in how far the character of the beverage may be modified by certain simple alterations in the methods of distillation. It is evident that by increasing the amount of heads to be returned to a future charge, the acidity would be very slightly raised,

[21] For a complete study of the products of distillation, see Tolman, *Bull. U. S. Dept. Agr. Bur. Chem.* (1910), 130, 127.

while the content of higher alcohols, esters, and aldehydes would be rendered appreciably less, and that by increasing the amount of tails the resulting product would run somewhat higher in higher alcohols, esters, and aldehydes and considerably lower in acids. Several examples are given in illustration of these principals in Table IX. Number 1 represents the analysis of the distillate as actually obtained by the method employed at the distillery, number 2 the analysis of the distillate which would be obtained by increasing the heads to 13 liters or one per cent of the charge, and number 3 the analysis of the distillate resulting from increasing the heads to 23 liters and the tails to 77 liters. In this last case, 20 liters of water have been added to lower the proof so that a better comparison with the other liquors might be had.

TABLE IX.—*Illustrating the effect of the removal of heads and tails on the composition of vino de coco.*

Sample number.	Description.	Alcohol.	Acids.	Esters.	Aldehydes.
		Per cent.			
1	Heads 2 liters, tails 17 liters	37.24	219.2	287.4	5.4
2	Heads 13 liters, tails 17 liters	36.04	222.6	192.1	4.5
3	Heads 23 liters, tails 77 liters	37.24	173.4	171.7	4.1

The third liquor, although of the same type as the first, contains in comparison with it considerably smaller amounts of secondary distillation products, or, in other words, has undergone a partial rectification. The determination of higher alcohols in liquors abnormally high in esters and aldehydes, unless by special methods, is inaccurate and unsatisfactory, hence the figures given in Table VIII for higher alcohols are untrustworthy as regards the first few fractions and can not be used in calculating the degree to which these constituents may be eliminated by fractionation. However, it is evident that the rejection of the first fraction lowers the content of higher alcohols in a considerable degree. The heads and tails would be reserved for future utilization, and practically no alcohol would be lost.

Since it was considered advisable to verify the results obtained at Nagcarlan by an investigation of another distillery in another district, two distillations were supervised at Cota, Tayabas Province, with the assistance of Internal Revenue Agent Hoey, on July 30 and August 1, 1911.

The still at Cota is an old one, about to be replaced, of a type practically

identical with that employed at Nagcarlan. However, in a number of particulars the equipment and methods are superior. A tank of sufficient size to hold the charge next to be distilled, in trade terms a "wash-warmer" is placed between the still and the condensing worm, and the vapors of the charge undergoing distillation are carried through a coil set into this tank. At the end of a distillation, when the old charge is drawn off, the new one may be run in at once without waiting for the still to cool and the new distillation begun in a comparatively short time. In this way an economy of time and fuel is effected and the tank at the same time serves as an auxiliary condenser.

At this distillery it is not customary to remove any heads, and the whole distillate is collected in a small mixing tank where it may be measured and a proof reading taken from time to time until a liquor of the desired strength has been obtained. The tails are then collected so long as any appreciable amount of alcohol continues to come over. An attempt is made to conduct the distillation at a comparatively low temperature, and the distillate as it comes from the condensing worm is kept thoroughly cooled to avoid subsequent loss of alcohol.

Our first run was made with a clean still into which 1,140 liters of fermented coconut sap were introduced; no heads, tails, or residue from the previous distillation were present.

With this distillation as with the next to be described samples of the still contents before and of the residue after distillation were taken and analysed, but the analyses must be considered of doubtful accuracy and have been omitted. The following fractions were sampled:

	Liters.
Heads	15
Beverage No. 1	125
Beverage No. 2 (inclusive of Beverage No. 1)	180
Tails	15

The analyses are given in Table X.

TABLE X.—*First distillation of vino de coco at Cota.*

Sample.	Alcohol.	Acids.	Esters.	Higher alcohols.	Alde-hydes.
	Per cent.				
Heads	59.1	172.2	2,129.0	1,179.2	5.3
Beverage No. 1	48.1	217.2	218.5	48.8	2.3
Beverage No. 2	a 41.2	255.6	192.4	38.3	2.2
Tails	9.7	391.2	112.7	18.7	1.9

a Somewhat uncertain.

It will be seen that in all essential respects these figures corroborate those obtained at Nagcarlan, and, inasmuch as all stills throughout the Islands employed for the distillation of *vino de coco* are of the same general type, the data obtained may safely be considered as fairly representative.

Therefore, it may be considered as demonstrated that the

practice of removing a considerable amount of heads and tails will affect the composition of the distillates in a manner similar to that indicated by the results obtained at Nagcarlan, and the question of the disposal of these fractions must receive consideration.

If these are returned to the following charge of *tuba* for redistillation, it is evident that the ester and to a lesser degree the higher alcohol and aldehydes content of the charge will be raised and the ensuing distillate will be somewhat higher in those constituents. This effect would be in a certain degree cumulative, and in actual practice the distillates would become more and more impure, although probably a point would be reached beyond which the contamination would not increase. With regard to the esters, the consideration of which is of more importance than the other constituents, this difficulty could easily be remedied by the treatment of the heads with an alkali. Under normal conditions when 15 liters of heads are taken from a distillation of from 1,100 to 1,300 liters, this fraction contains about 25 grams of acids and 350 grams of esters, and would theoretically require about 123 grams of lime to effect the neutralization of the acid and the hydrolysis of the esters. For practical purposes a partial saponification, by which the major portion of the esters are eliminated, would be sufficient to prevent any increase of esters. We are of the opinion that were some such treatment given to the heads, this practice of returning considerable amounts of heads and tails to the next charge would work out in a satisfactory manner, and the desired result to be secured by a partial rectification of the *vino de coco* would not in any considerable degree be sacrificed, but this could only be proved by the results of continued distillery practice.

The better procedure would be for the distiller to dispose of his heads to the rectifier, either directly or by working them into distillates to be sold as crude alcohol rather than *vino de coco*.

A second distillation was made with 1,140 liters of fermented coco sap, 15 liters of heads, 45 liters of tails, and 117 liters of residue in the still from the previous charge, making a total of 1,317 liters. The heads had been treated with 150 grams of lime and allowed to stand over night before introduction into the still.

The following fractions were taken:

	Liters.
Heads	15
Beverage No. 1	165
Beverage No. 2 (inclusive of Beverage No. 1)	174
Tails	37

The analytical results are given in Table XI. The analyses of the still charge and of the residue have been rejected as somewhat untrustworthy.

TABLE XI.—*Second distillation of vino de coco at Cota.*

Sample.	Alcohol.	Acids.	Esters.	Higher alcohols.	Alde-hydes.
	Per cent.				
Heads	57.5	167.3	1,982.0	1,713.0	5.5
Beverage No. 1	46.2	196.8	226.4	54.2	2.4
Beverage No. 2	44.6	208.2	192.7	52.9	2.0
Tails	19.3	279.9	106.4	17.2	1.4

As was to be expected these results differ in no essential respect from those obtained in previous distillations.

Rough approximations of the efficiencies of the two distilleries have been made indicating the failure to obtain in the distillate from 10 to 20 per cent of the alcohol present in the *tuba.* The loss during distillation owing to leakage and evaporation is slight; practically the entire amount is due to incomplete distillation. The residue at these distilleries normally appears to contain between 0.1 per cent and 0.4 per cent of alcohol.

THE POTABILITY OF PHILIPPINE DISTILLED BEVERAGES.

THE POT-STILL BEVERAGES.

It is the generally accepted belief among the white residents of the Philippine Islands that the use of native distilled beverages is attended with very deleterious physiological effects, attributable to the presence of certain "poisonous" substances among which "fusel oil" and wood (methyl) alcohol are often specified.

It is hardly necessary to state that methyl alcohol does not occur in any distilled liquors of the Philippines or elsewhere, unless it has been added to the finished product in wilful adulteration. None has ever been detected in any native beverage.

It may be seen from the analyses given that "fusel oil," a term applied to the alcohols higher in order than ethyl alcohol. is found in liquors of local manufacture in amounts which are notably smaller than in similar imported liquors of pot-still type.

The average content of aldehydes (and also of furfurol) is by no means abnormal.

In fact the only respect, so far as may be determined by chemical analysis, in which this class of distilled beverages may

be considered abnormal is their comparatively high content of acids and esters.

Very little is at present known in connection with the question of the relative toxicity of different distilled liquors. There have been numerous investigations of the harmfulness of higher alcohols, esters, aldehydes, etc., but not under conditions simulating those of the use of alcoholic liquors during long periods.

It is well known that the total poisonous effects of liquors are not entirely due to alcohol, but in part to secondary fermentation and distillation products, and it is for this reason that two different liquors give rise to an intoxication of distinctly different types.

Nevertheless, and especially with distilled liquors, it is unquestionably true that alcohol is the preponderatingly harmful ingredient.

Therefore, the question of the harmfulness of the use of any distilled liquor becomes largely one of its alcoholic content and of the amount imbibed, and it is generally agreed that the consumption of *vino* by the habitual vino drinker is very great, owing to the fact that it is everywhere available and that it is very cheap, and possibly also to the fact that comparatively large amounts may be imbibed before its physiological effects begin to be felt.

In our opinion it is the immoderate consumption rather than the unwholesome composition of Philippine distilled liquors which is responsible for their ill-repute.

BEVERAGES MADE FROM RECTIFIED ALCOHOL.

There is no reason for questioning the wholesomeness of the more carefully made Philippine gins or of certain other distilled liquors and liqueurs, the manufacture of which involves a considerable degree of rectification of the spirits, when they are compared to imported beverages. The foregoing analyses show that the differences in composition of the alcohol forming the basis of these beverages is negligible.

THE IMPROVEMENT OF THE POT-STILL BEVERAGES.

With regard to the improvement of Philippine liquors, it is unquestionably true that the selection of pure materials and the adoption of cleanly methods and sanitary surroundings are factors which will reduce undesirable fermentations [22] and be conducive to the production of the best beverages in the most economical manner. In this respect there is a wide divergence at the different distilleries in these Islands, but the Bureau of Internal Revenue has already effected a vast improvement.

It may also be assumed that such modifications in the methods

[22] At the earliest opportunity, a study of the fermentation changes in palm saps will be undertaken, a matter of considerable practical importance as well as of scientific interest.

and apparatus of distillation, as will result in a more thorough rectification of the product, will, in general, be advantageous. While some question exists as to the harmfulness of the presence of comparatively large amounts of acids and esters, it is well to reduce the amount of these ingredients so far as may be accomplished in a practical manner without altering in any essential respect the nature of the beverage. When the liquor is to be sold as a beverage in distinction from that portion of the liquor which is supplied as crude alcohol to the rectifiers, it is reasonable to demand that it shall conform to certain specifications of alcoholic strength and purity. At present, *vino de coco* is sold of grades varying from 60 per cent to 100 per cent proof, and contains very variable amounts of secondary distillation constituents. There was, at the beginning of this work, no recognized standard of purity for this product.

We believe that the beverages distilled in pot stills, from fermented palm saps, are of such quality, flavor, and merit, when properly made, that they might be properly bottled and labeled and then find a better market in the Philippines and be the medium of considerable export business of great benefit to the owners and operators of nipa and coconut groves.

With the view of improving the character and of establishing standards and extending the market for this class of beverages, the questions involved were laid before the Collector of Internal Revenue, and, later, before the Food and Drug Board of the Philippine Islands.

The principal questions were the labeling, standards, methods of manufacture, and storage.

Labeling.—The name *vino* or *bino* must be discarded for two reasons, (*a*) the beverages are not wines and (*b*) a great local prejudice has arisen against anything which is known as "native drink" or *bino*. The name "whisky" can not be employed for it is contrary to the decisions under the United States Food and Drugs Act. The name "rum" does not seem to be applicable for the reason that, while the beverage is made from fermented sucrose or materials from which sucrose can be refined, it has not the general characteristics of rum as now found upon the markets. The name "brandy" was adopted for the following reasons. Brandy is not defined by any standards adopted by the United States. It is usually defined and believed to be the distillate of fermented fruits of various kinds, such as grapes, peaches, blackberries, apples, etc.

The Century Dictionary defines brandy as "A spirituous liquor obtained by the distillation of wine, or of the refuse of the wine-press. The average proportion of alcohol in brandy ranges from 48 to 54 per cent. The name *brandy* is now given to spirit distilled from other liquors, and in the United States to that which is distilled from cider and from peaches. * * *

British brandy, a common kind of brandy distilled in England from malt liquors, and given the flavor and color of French brandy by artificial means."

In arguing for the use of this term for these beverages, it is to be remembered that for hundreds of years in the Philippines and other countries the beverages made from fermented palm saps without distillation have been known as "palm wines" and that a beverage made by distilling wine is entitled to be called brandy.

The names proposed are "Philippine Palm Brandy" with the proper designations as "Philippine Coco Palm Brandy," "Philippine Nipa Palm Brandy," etc.

Standards.—The following standards were proposed to the Food and Drugs Board of the Philippine Islands and adopted after notification of all interested persons, discussion at a public hearing, and after consideration of documents submitted.

(1) $\left\{ \begin{array}{l} \text{Coco} \\ \text{Nipa} \end{array} \right\}$ Palm Brandy; (2) Philippine $\left\{ \begin{array}{l} \text{Coco} \\ \text{Nipa} \end{array} \right\}$ Palm Brandy;

(3) $\left\{ \begin{array}{l} \text{Old or} \\ \text{Aged} \end{array} \right\}$ Philippine $\left\{ \begin{array}{l} \text{Coco} \\ \text{Nipa} \end{array} \right\}$ Palm Brandy.

(1) $\left\{ \begin{array}{l} \text{Coco} \\ \text{Nipa} \end{array} \right\}$ Palm Brandy is the spirit distilled from the properly fermented sap drawn from the inflorescence of the $\left\{ \begin{array}{l} \text{Coconut palm } (\textit{Cocos} \\ \text{Nipa palm } (\textit{Nipa} \end{array} \right.$ *nucifera* L.) *fruticans* Wurmb.) $\left. \begin{array}{l} \end{array} \right\}$ from a pot still with or without the employment of a doubler, without the addition of any substance, and shall contain not less than 40 per cent (80 proof) alcohol and not more than 50 per cent (100 proof) alcohol; not less than 300 or more than 600 grams of secondary products of distillation congeneric with ethyl alcohol; not less than 100 or more than 250 grams of volatile acids (as acetic); not less than 100 or more than 300 grams of esters (as acetic ether); not more than 150 grams of fusel oil (higher alcohol), and not more than 10 grams of aldehydes (as acetic aldehyde) to 100 liters of 100 proof spirits.

(2) To be entitled to use the word "Philippine" in describing the coco or nipa palm brandies, the beverage must be made in the Philippines from the product of palms growing on the Islands.

(3) To be entitled to use the prefix "old" or "aged," the palm brandy shall conform to the above standards at the time of distillation and shall have been stored in wooden casks or barrels for a period of not less than three years prior to its removal from the warehouse for consumption and shall be diluted to the proper proof with pure distilled water.

Nothing in these standards shall be construed to forbid the bottling and sale of beverages of lower alcoholic (proof) content than specified by the standards, but only beverages conforming to the standards shall be labeled "Palm Brandy."

Methods of manufacture.—Certain modifications of the present methods of distillation are advocated, which will result in a partial rectification of the spirits, making it easy to comply with the proposed standards. Excess of acids is prevented merely by maintaining the grade of 90 per cent proof. The influence of the effect of the grade of palm brandy on the acid

and ester content is well illustrated by the following figures, which are the average of the results obtained in the previously described investigations of *vino de coco* of pot-still manufacture.

Alcohol (per cent).	Acids.	Esters.
32.5	417	226
36.6	364	272
45.2	248	363

The figures for acids and esters represent grams per hundred liters of proof spirits.

For the reduction of the ester content, the removal of a first fraction of heads is suggested. It has been shown that a very considerable reduction is effected when the volume removed is about 1 per cent of the total charge, but better results would be obtained by increasing this to 1.5 per cent.

The following suggestions are made for the distillation of charges of from 1,100 to 1,300 liters.

Remove the first 20 liters of heads, and then collect the distillate until the grade falls to a little over 90 proof. The tails are then to be collected so long as enough alcohol continues to come over to make it advisable, probably somewhat longer than is the present practice in most distilleries. The tails may be added to a later charge without ill effects, but the heads should be treated with about one-half kilogram of lime and left at least twelve hours before being used in any distillation of a beverage and should preferably be disposed of as crude alcohol.

It is believed that the adoption of these modifications will result in a more uniform and better grade of beverage and eliminate the occurrence of distillates of abnormal composition without appreciably increasing the expense of manufacture or modifying in an adverse manner the characteristic flavor of the beverage.

Storage.—Finally, it may well be possible to effect improvement in Philippine liquors by some of the methods commonly employed in other countries for the treatment of distilled liquors after distillation. With the exception of gin, which in comparison with other spirits is given a thorough rectification, and a certain amount of liquor of illicit manufacture, practically all liquors are given some after-treatment. The newly distilled liquor is considered comparatively unwholesome, and has an inferior and usually a disagreeable flavor and odor.

On the other hand, pot-still *vino de coco* and *vino de nipa* have an agreeable flavor when newly distilled, and, so far as we are aware, are always consumed immediately or after a certain period of storage in glass containers. It is well known that distilled liquors undergo no improvement through storage

in glass, while it is universally admitted that aging in wood is highly beneficial with most liquors.

An investigation of this question with reference to Philippine palm brandies was begun about a year ago. The first samples which were put in storage were prepared before the experimental work, previously described, was completed, so that the prescribed methods of distillation were not followed, and accurate data regarding them are not available.

From now on, the Bureau of Internal Revenue proposes to put one barrel of *nipa* and one barrel of *coco palm brandy,* made by prescribed methods, in storage every six months. Analyses of these products will be made at the time of storage and every six months thereafter.

The data so far available are as follows:

TABLE XII.—*Description of palm brandies now in storage.*

Bar-rel No.	Palm brandy.	Date of distillation.	Proof.	Still charge.	Heads.	Tails.	Residue in still.	Beverage.	Distillery number and location.
				Liters.	Liters.	Liters.	Liters.	Liters.	
1	Coco	Apr. 22, 1911	100						A-1-585; Majayjay.
2	Nipa	Dec. 14, 1910	100						A-1-633; Dagupan.
3	Coco	Oct. 11, 1911	103	720	7	35	600	78	A-1-585; Majayjay.
4	Nipa	Nov. 23, 1911	88	1,150	a 10	175	895	70	A-1-633; Dagupan.

a 96 proof.

TABLE XIII.—*Analyses of palm brandies now in storage in charred barrels.*

Bar-rel No.	Sample removed for analysis.	Duration of storage.	Color. a	Density 15°.	Alcohol.	Total acids.b	Volatile acids.b	Esters.b	Higher alcohols.b	Aldehydes.b	Solids.b
					P. ct.						
1	July 24, 1911	3 months	Y Normal	0.9326	50.0		190.2	163.0	78.5	16.5	27.5
1	Jan. 24, 1912	9 months	O Y Shade 1 c	0.9274	50.2	212.0	204.2	335.8	122.8	15.7	66.7
2	July 24, 1911	7 months	O Y Shade 1	0.9338	48.5		152.0	310.5	59.9	10.25	72.5
2	Jan. 24, 1912	13 months	O Y Shade 1 d	0.9253	50.8	165.0	153.0	279.1	83.5	6.9	98.8
e 3	Oct. 11, 1911	3 days	Colorless	0.9330	51.6	147.0	146.0	336.0	136.0	none	5.0
3	Apr. 9, 1912	6 months	Y O Shade 1 f	0.9315	51.9	170.2	162.0	241.0	65.0	1.1	108.9
4	Dec. 12, 1911	19 days	Y Shade 2 g	0.9461	41.75	184.5	172.7	363.0	153.0	17.8	67.0

a Not having a Lovibond colorimeter available, the color comparisons are made by means of the Bradley Color Standard [Milliken, Identification of Pure Organic Compounds. John Wiley & Sons, London (1905), 1, 232], by comparison with layers of liquids about 10 centimeters deep.

b Expressed as parts per 100 liters of 100 proof spirits.

c 8.8 centimeters layer.

d 6.6 centimeters layer.

e Analysis by E. R. Dovey.

f 8.4 centimeter layer.

g 15.0 centimeter layer.

The investigations of the effects of storage will be continued, and the results made available from time to time.

Pending the completion of this work, a storage period of three years was adopted as a minimum for the reason that it seems reasonable that in this climate, with the uniform high temperature, the desired result will be attained in this time. The Bureau of Internal Revenue will furnish instructions regarding storage warehouses, and has promulgated rules to assist the distillers in manufacturing the beverages.

Numerous methods have been proposed for hastening the maturing of liquors and have been employed with a greater or lesser degree of success. Perhaps the most successful of these consists in the filtration of the new distillate through wood charcoal, followed by a comparatively brief period of aging in wood, after the manner in which considerable amounts of so-called "Tennessee" whisky are now manufactured. Such a filtration has been shown to remove completely the furfurol and oily matter present and to reduce to a certain extent the amounts of other secondary distillation products, notably acids, eliminating the disagreeable flavor and odor of the new whisky.

By a similar process on a very small scale, a sample of Philippine Coco Palm Brandy, superior in our opinion to the unfiltered product, was made at this laboratory.

We are of the opinion that further experimentation with regard to the fermentation, distillation, and maturation of Philippine distilled beverages and the practical application of the information here made available would result in modifications of composition, flavor, and aroma and an improved product which would appeal to a larger and more discriminating class of consumers both in domestic and foreign markets, and that such experimentation would, in the end, prove highly remunerative to the distillers.

ILLUSTRATIONS.

PLATE I.

A primitive still called *caua*. For a long time this was the standard type of apparatus used in the Philippines, but now it is only used for illicit distillation. (Photograph loaned by Bureau of Internal Revenue.)

PLATE II.

A primitive distillery in the nipa district of Pangasinan Province near the Gulf of Lingayen. The photograph shows the copper pot, tubs containing condenser and condenser water, and two natives in the act of filling the still for a run. The earthen vessels used for transporting *tuba* are on the floor. (Photograph by Cortes.)

PLATE III.

The exterior of the same distillery, showing the drawing of water for the condenser, by hand, from a well at the river-bank, and the pipe for conducting the water to the condenser. (Photograph by Cortes.)

PLATE IV.

The interior of the storage room of the same distillery, showing the storage barrels for alcoholic beverages, fitted with gauge glasses. (Photograph by Cortes.)

PLATE V.

Rectifying apparatus and boiler in plant of Ayala and Company, Manila, made by D. Savalle, Fils et Cie., Paris.

PLATE VI.

View of the plant of Ynchausti and Company, Manila, from the water-front. The other side of the building fronts on Calle Tanduay. This distillery has the largest capacity of any plant in the East. The unloading of the *cascoes* is shown. These *cascoes* are fitted with iron storage tanks holding from 16,000 to 20,000 liters and are used for transporting alcohol from the Bulacan-Pampanga district across Manila Bay. (Photograph by Martin.)

PLATE VII.

A rectifying still in Ynchausti and Company's plant, manufactured by Désiré Dubois, Bruxelles. Capacity 25,000 liters. This still can handle 300,000 liters per month, producing 150,000 liters of 185 proof alcohol. (Photograph by Martin.)

PLATE VIII.

One of the storage rooms of Ynchausti and Company, having a capacity of 150,000 liters. The total storage capacity of this distillery is about 1,000,000 liters. (Photograph by Martin.)

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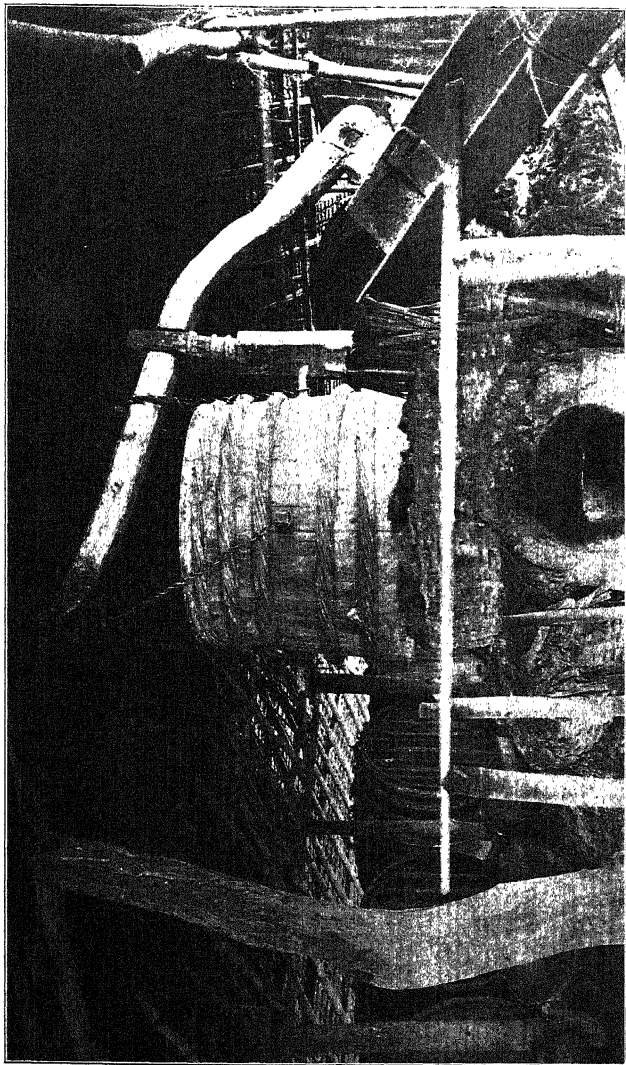
PLATE I. A PRIMITIVE STILL CALLED "CAUA."
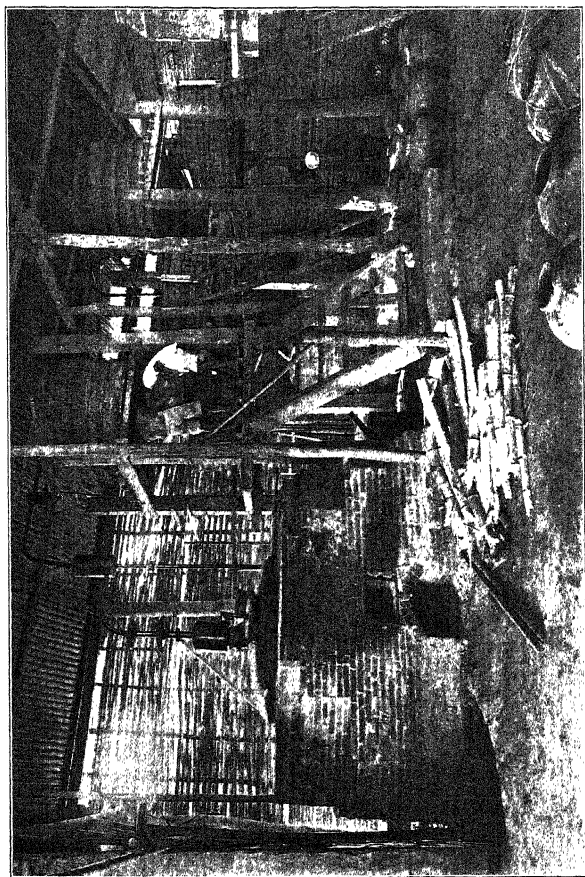
PLATE II. A PRIMITIVE DISTILLERY IN PANGASINAN PROVINCE.
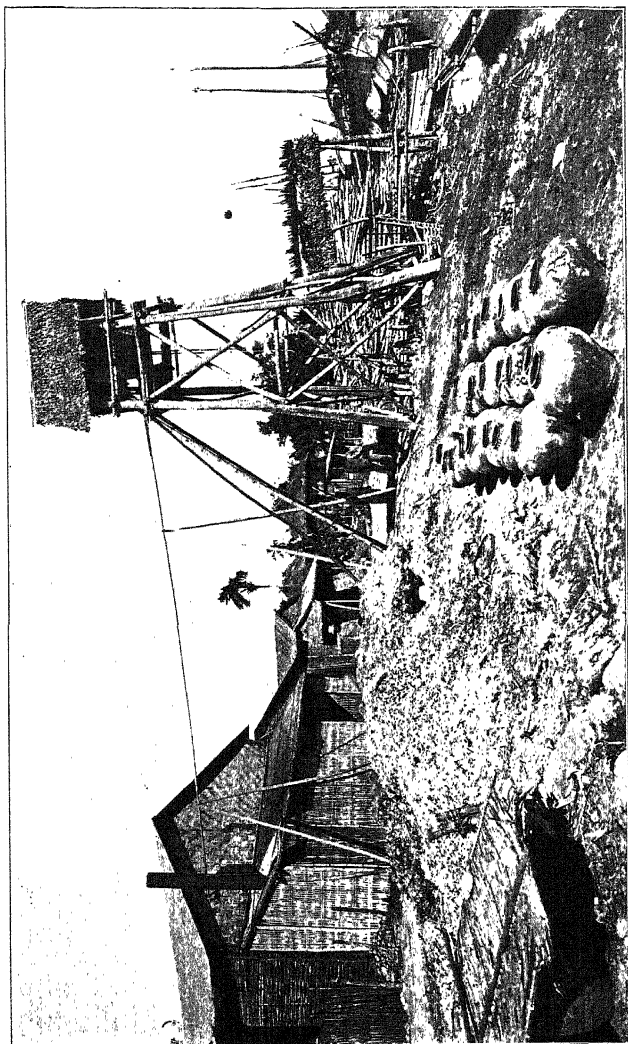
PLATE III. EXTERIOR OF PRIMITIVE DISTILLERY IN PANGASINAN PROVINCE.

PLATE IV.   INTERIOR OF STORAGE ROOM IN PRIMITIVE DISTILLERY.
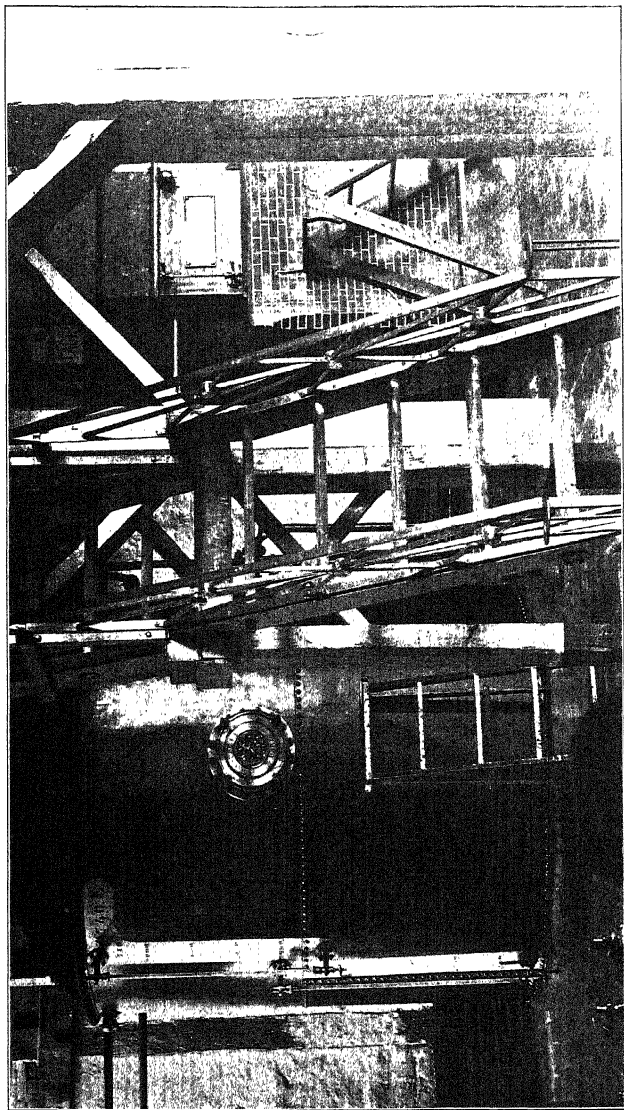
PLATE V. RECTIFYING APPARATUS AND BOILER IN PLANT OF AYALA AND COMPANY.
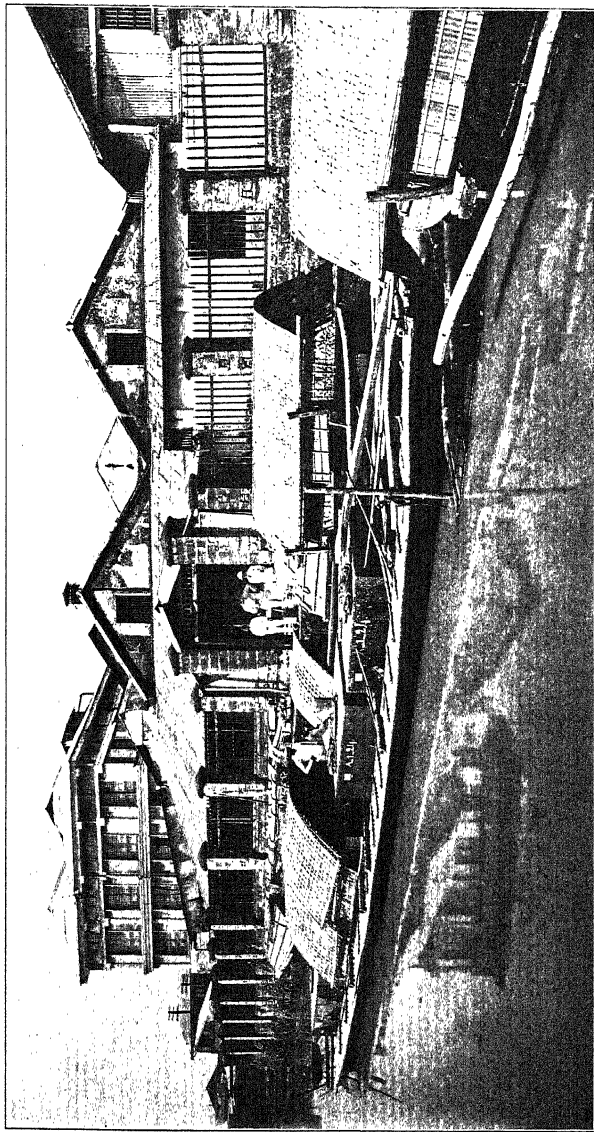
PLATE VI. PLANT OF YNCHAUSTI AND COMPANY, MANILA.
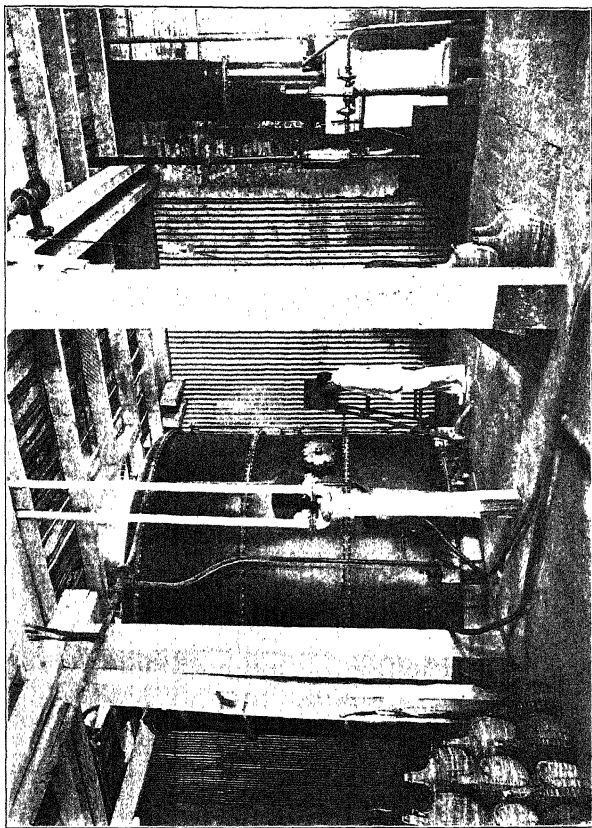
PLATE VII. A RECTIFYING STILL IN YNCHAUSTI AND COMPANY'S PLANT.
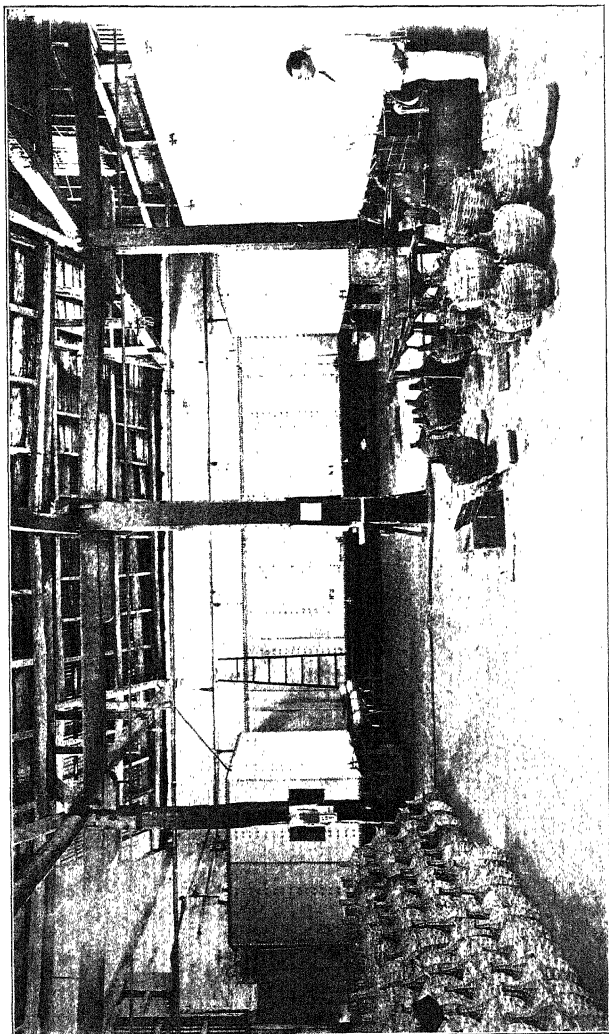
PLATE VIII. ONE OF THE STORAGE ROOMS OF YNCHAUSTI AND COMPANY.

SOJA-BEAN CURD, AN IMPORTANT ORIENTAL FOOD PRODUCT.

By H. D. GIBBS [1] AND F. AGCAOILI.

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

The soja-bean, *Glycine hispida* Maxim,[2] is constantly receiving greater recognition and appreciation as an important nitrogenous food, its use having heretofore largely been confined to the countries where rice is the principal article of diet, especially to China and Japan. The employment of this food is rapidly extending, and its value is becoming appreciated in other countries of the world, even where a lack of nitrogenous food is not felt.

A large variety of products are made, among which may be mentioned flour, bread, sauce, milk, cheese, and preserves, and the casein can be used industrially in painting, for the preparation of products where the resistance to moisture is desired, in paper sizing, and in a number of other preparations.[3]

Many analyses of the beans are to be found in the literature, and a considerable variation is to be expected in the composition. The following represent the usual limitations:

[1] Associate professor of chemistry, University of the Philippines.

[2] For the botanical history, varieties, and field studies of this plant, see *Bull. U. S. Bur. Pl. Indust.* (1910), 197.

[3] For late articles on the subject see Beltzer, *Rev. chim. ind.* 22, 209, through *Chem. Abstracts* (1911), 5, 3597, and H. van der Waerden, *Pharm. Weekblad* 48, 889 through *Chem. Abstracts* (1911), 5, 3737, and the present magnitude of the soy-bean industry see Lewkowitsch, *Chem. Ind., Berlin* (1910), 33, 705.

TABLE I.—*Analyses of soja-beans.*

Constituent.	Usual variations found in the literature. [a]	Our analyses of *Glycine hispida* Maxim.
	Per cent.	*Per cent.*
Water	9 to 13	9.84
Protein	31 to 42	37.53
Fat	14 to 22	18.97
Nitrogen-free extract	27 to 31	
Crude fiber	4 to 13	
Starch	trace to 3.5	
Ash	4.7 to 5.9	4.79
Nitrogen		5.99
SO₃, per cent in ash		1.4
Oil refraction Zeiss Butyro scale at 30°.5		81.0
Iodine number Hanus		66.3

[a] König, Chemie der menschlichen Nahrungs-und Genussmittel, Berlin (1903), **1**, 598; (1904), **2**, 789; Inouye, *Bull. Col. Agr.*, Tokyo (1895), **2**, 209; Pellet, *Compt. rend. Acad. Sci.* (1880), **90**, 1177.

Eighty-five to 90 per cent of the nitrogenous substances is in the form of pure protein and 10 to 15 per cent is not proteins. Meissl and Böcker [4] give the following analyses:

Constituent.	Per cent.
Water	10.0
Soluble casein	30.0
Albumin	0.5
Insoluble casein	7.0
Fat	18.0
Chloresterin, lecithin, resin, and wax	2.0
Dextrin	10.0
Starch	5.0
Cellulose	5.0
Ash	5.0

Stingl and Morawski [5] found only a little starch and dextrin but considerable quantities of an active diastase. They state that the various sugars are about 12 per cent. Inouye has confirmed the absence of starch in the Japanese soy-beans. Osborne and Campbell [6] state that the chief proteid is glycinin, a globulin which is precipitated by dilute acids and lime salts, and that the precipitates are soluble in sodium chloride solutions.

[4] *Sitzungsber. Akad. d. Wiss. math.-nat. Klasse*, Wien (1883), **87**, 372, 391.

[5] *Chem. Centralbl.* (1886), **17**, 724.

[6] *Journ. Am. Chem. Soc.* (1898), **20**, 419.

Blin[7] gives an analysis of soy-bean meal used in Germany
and Austria, for fattening hogs, as follows:

Constituent.	Per cent.
Water	10.60
Nitrogen	7.28
Protein	45.50
Oil	7.61
Non-nitrogenous organic	30.39
Mineral	5.90

One of the most important foods manufactured from the soy-
bean is the curd which is sold in the form of small cakes. The
Chinese have introduced and extended the use of this product
throughout the East, and Bloch states that there is no Chinese
settlement without one or two bean-cheese factories.

This curd is known by a number of different designations.
In English it is often spoken of as "bean-cake" or "bean-cheese,"
although it is not entitled to the designation "cheese," since no
ripening process takes place in its manufacture. Attempts have
been made to manufacture a cheese from the bean-cake by means
of inoculation with bacteria.[8] Among the natives of the district
of the Philippine Islands surrounding Manila, it is called *toqua,*
a name of Chinese origin. In China the substance is known as
teou-fou[9] and *tao-hu*[10] and in Japan as *topu.*[11]

In this district, so far as observation has extended, the manu-
facture is carried on entirely by Chinese practically in the
manner described by Bloch and Geerligs,[12] except that methods
have been introduced which border on adulteration.

The soja-bean, *Glycine hispida* Maxim, is imported into the
Philippines from southern China in large quantities, principally
from Amoy and Hongkong. In the markets of the latter place
they are known as "soy-beans" or *pak-tau.*

The process of manufacture of bean-curd in this locality is
briefly described as follows:

"The beans are soaked in water or in a salt solution,[13] during which

[7] *Chem. Abstracts* (1911), 5, 1952.

[8] Katayama, *Bull. Col. Agr.,* Tokyo (1906-8), 7, 117.

[9] Bloch, *Ztschr. f. Untersuch. d. Nahrungs.-u. Genussmittel* (1906), 12,
564.

[10] König, *ibid* (1904), 2, 789.

[11] *Ibid.*

[12] *Ibid,* 790; *Rec. U. S. Dept. Agr., Off. Exp. Sta.* (1896-7), 8, 72.

[13] Analysis of a salt solution which was being added when the sample
was taken showed 27.8 per cent sodium chloride.

GIBBS AND AGCAOILI.

process pronounced swelling takes place, and they are then ground by hand between two millstones. The white, creamy liquid which flows from the grinder is ladled into a large caldron and there slowly boiled and coagulated into a white curd.

The addition of gypsum water, or sea water containing magnesium chloride, is mentioned by various writers as necessary for the coagulation of the bean-curd.

Inouye states that it seems most probable that insoluble calcium and magnesium salts of casein are precipitated from solutions of the sodium or potassium salts which are not precipitated by boiling, and the work of Osborne and Campbell bears out this statement.

The curd is ladled out and small quantities formed into cakes about 8 by 8 by 3 centimeters, by folding into a small cloth. The cakes, each one still being wrapped in its cloth, are then pressed in a hand press to expel much of the solution. After removing the cloths they are baked slightly and then are ready for sale. The baking is not sufficient to harden the cakes to any great extent, and in appearance the interior is unchanged from the original white, while the exterior is light brown.

Bloch states that 6 kilograms of beans give about 80 liters of coagulable liquid, which will produce 20 to 25 kilograms of cheese or 13 kilograms of pressed cakes.

TABLE II.—*Analyses of the cakes.*[a]

Constituent.	Bloch.		Geerligs, cheese, tao-hu.	König, tofu.	Our analyses of the baked cakes toqua.	
	Cheese.	Pressed cakes.				
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Water	83.85	88.75	76.15	84.81	73.0	72.1
Protein	11.25		13.15	7.41	13.88	17.56
Nitrogen	1.296	0.248			2.22	2.81
Fat	4.33	0.04	7.09	5.25	10.78	10.99
Ash	0.57	0.36	b2.21	1.08	1.2	1.27
Ash:						
Sodium chloride					0.00	0.00
SO₃ in combination					0.66	0.66
Oil:						
Refraction, Zeiss butyro scale at 29°. 5					86.0	86.0

[a] Many other analyses are to be found in the literature.
[b] With 0.97 per cent sodium chloride.

The same food product, known locally under the name *tahuri* or *tahuli,* is imported from southern China in large stone jars. It is preserved by covering the cakes with a strong salt solution. During shipment, the cakes are somewhat broken, giving to the liquid portion the appearance and consistency of an emulsion. The two portions of the mixture were analysed separately.

. TABLE III.—*Analyses of tahuri or tahuli.*

Constituents.	Solid.	Liquid.
	Per cent.	*Per cent.*
Water	55.76	57.86
Protein	14.56	9.56
Nitrogen	2.33	1.53
Fat	7.12	2.09
Sodium chloride	12.7	16.38
SO₃	0.08	0.007
Fat: Refraction, Zeiss butyro scale, at 28. °5	82.5	

Adulteration.—No mention of methods of adulteration of this cheap food product has been found in the literature. Upon the local markets it has been discovered that powdered gypsum was mixed with the cheese before baking the cake and also with the liquid before coagulation. In some cases the amounts added were so small that the purpose was evidently not to increase the weight or bulk, but for the coagulation of the curd as previously suggested by other writers, and also, perhaps, for increasing the firmness of the cakes. The salt solution in many of the imported shipments is colored red by means of a wood or by a vegetable dye.

The local manufacturers are prohibited from using coloring matter or powdered gypsum. Dilute solutions of calcium or magnesium salts are not considered objectionable. Where a binder is desired to give the cakes greater firmness, starch or gelatine is employed.

ILLUSTRATION.

PLATE I. CHINESE BEAN-CURD FACTORY IN MANILA.

REVIEWS.

The fact that this work is now in its tenth edition is evidence of its popularity and usefulness. In character the last edition is like the previous ones, that is, the Handbook is in reality a guide to volumetric analysis, useful for the analytical chemist to have in his desk during work, but if the analyst wishes more than mechanically to prepare his task, he must have access to an extended chemical library, and in addition have a good grounding in general chemistry to enable him, by his own resources, to develop existing methods and devise new ones. The fundamental basis of the various volumetric processes is not dwelt upon in this work, but in many instances is given by literature references, so, for example, the theory of indicators is not explained, but reference is simply made to a rather elementary textbook discussing the subject. It would therefore be more advisable, for class room work, to cover a few processes and these with a thorough general discussion of the principles of the subject, than to expect students to follow out many processes which they are expected to memorize only. However, once the applications of general chemistry to volumetric analysis are comprehended and the student enters upon actual commercial work, the volume in question will be most useful to have at hand at all times.

P. C. F.

The contents and purpose of this book are best described in the author's introduction as follows:

(1) To describe briefly the principal foodstuffs and the agencies and processes through which they become available for the uses of the body; (2) to follow their functions in the tissues

and their fate in metabolism; (3) to determine the food requirements of the body under different conditions; (4) to ascertain the functions of the individual chemical elements in nutrition and the quantities in which they should be supplied by the food; (5) to consider the criteria by which we should judge the nutritive value and economy of articles of food.

Doctor Sherman is an expert in this subject, and has drawn on many sources and several sciences for his facts. The result of recent work on the polypeptides by Emil Fischer and others has been concisely treated in so far as it affects the subject of foods. In the physiological and nutrition experiments quoted, besides the results, sufficient information is given in many cases to enable the experiments to be repeated or to suggest lines on which to carry out further work. The tables of nutrition values of various foods will be found of considerable value, summarizing a great many facts in a small space.

In some of these tables, there is a tendency to carry the accuracy of the expressed result beyond the accuracy of the data. For example: Considering the great variation in the ratio of edible to nonedible matter in such substances as Brazil nuts, fowl, ham, etc., it is useless to express the nutritive value to four significant figures.

However, the book, as a whole, is an eminently readable one and will be found of great assistance to all who are called upon to solve problems of a dietetic nature.

E. R. D.

Paul C. Freer.

OBITUARY

Paul Caspar Freer

DIRECTOR OF THE BUREAU OF SCIENCE OF THE GOVERNMENT OF THE PHILIPPINE ISLANDS
DEAN OF THE COLLEGE OF MEDICINE AND SURGERY AND PROFESSOR OF
CHEMISTRY OF THE UNIVERSITY OF THE PHILIPPINES, AND
FOUNDER AND EDITOR-IN-CHIEF OF THIS JOURNAL

We are deeply grieved to announce the death of Doctor Freer at Baguio, Philippine Islands, on April the seventeenth, in his fifty-first year, from arterio-sclerosis and acute nephritis.

In an effort formally to express our sorrow and to honor his memory a memorial meeting of the members of the Staff of the Bureau of Science, the Council of the University of the Philippines, and the members of the Philippine Islands Medical Association will be held on July 1, 1912. The proceedings of this memorial meeting will be published in a future number of this Journal.

At a meeting of the members of the Staff of the Bureau of Science, held on the eighteenth day of April, the following resolutions were adopted:

Whereas it has pleased Almighty God in His Wise and Inscrutable Providence to remove from our midst Paul Caspar Freer, M. D., Ph. D., Director of the Bureau of Science of the Government of the Philippine Islands, since the time of its organization as the Bureau of Government Laboratories in the year 1901, Dean of the College of Medicine and Surgery, and Professor of Chemistry, University of the Philippines, and Founder and Editor-in-Chief of the "Philippine Journal of Science," who, for many years, has been our Leader, Counselor, and Friend; and

Whereas at best we can do little to indicate at this time our real appreciation of him as a man and as a worker for the general good: Therefore be it

Resolved, That we, the Members of the Staff of the Bureau of Science in Manila, Philippine Islands, do hereby express our deepest sorrow and keen feeling of personal loss in the death of Doctor Freer; and be it further

Resolved, That he holds a place of highest respect, admiration and appreciation both officially and personally in the hearts of all of us, and especially of those who were most intimately associated with him in scientific work; and be it further

Resolved, That it is the sense of the Members of this Institution that the Bureau of Science has suffered a very great loss and that the cause of Science in these Islands has been deprived of one of its most zealous and conscientious advocates; and be it further

Resolved, That we extend our sincere sympathy and condolence to his Widow in her overwhelming grief, to his Sister, Brother and other Relatives; and be it further

Resolved, That copies of these resolutions be engrossed and sent to the bereaved Widow and Brother of Doctor Freer, and that they be filed in the Archives of the Bureau of Science, transmitted to the Bureau of Civil Service, published in the forthcoming Number of each Section of the "Philippine Journal of Science," in the newspapers of Manila, in a paper in the City of Chicago, Doctor Freer's birth-place, and in "Science," the Official Organ of the American Association for the Advancement of Science, of which Doctor Freer was a Fellow.

For the Staff of the Bureau of Science:

RICHARD P. STRONG,
CHARLES S. BANKS,
E. D. MERRILL,
[L. S.] ALVIN J. COX,
OSCAR TEAGUE,
A. E. SOUTHARD,
       Committee.

At Manila, Philippine Islands, this eighteenth day of April,
in the year of our Lord one thousand nine hundred and twelve.

THE ACTION OF SUNLIGHT UPON METHYL ALCOHOL.

By H. D. GIBBS.[1]

(From the Division of Organic Chemistry, Bureau of Science, and the Department of Chemistry, University of the Philippines, Manila, P. I.)

CONTENTS.

I. THE ACTION OF SUNLIGHT UPON SOLUTIONS OF *p*-QUINONE IN METHYL ALCOHOL.

Ciamician[2] found that ethyl alcohol is oxidized to aldehyde in the presence of quinone and sunlight, and the quinone reduced to quinol. No action takes place in the dark. In the mother liquor from the purification of the quinol a small amount of an acid substance was found and Ciamician and Silber[3] state that there is also a small quantity of a brown-colored syrup. In the presence of sunlight some other quinones, and also some ketones and aldehydes, will produce the same result upon alcohol.

[1] Associate professor of chemistry, University of the Philippines.
[2] *Gazz. chim. ital.* (1886), 16, III.
[3] *Ber. d. deutschen chem. Ges.* (1901), 34, 1532.

Hartley and Leonard,[4] in connection with their work on the absorption spectrum of p-quinone, call attention to the powerful oxidizing properties of this compound upon polyhydric alcohols when submitted to the action of light. Since the quinol band shortly made its appearance, the use of ethyl alcohol as a solvent was precluded.

In this connection it is interesting to note that quinone in the presence of oxygen is more rapidly colored brown in the light than in the dark,[5] and that the shorter wave lengths are responsible for the effect. One gram of quinone in 20 cubic centimeters of ether showed no change in red light, and in blue-violet light formed long needles of quinhydrone in six hours.[6]

Since methyl alcohol is generally oxidized with greater difficulty than ethyl alcohol, it seemed of interest to study this solvent in connection with quinone, and I have found that methyl alcohol will produce the same result on exposure to sunlight in presence of p-quinone, the principal products formed being formaldehyde and quinol.

EXPERIMENTAL.

Quinone, purified by distillation in steam, was dissolved in methyl alcohol, 4 grams to 100 cubic centimeters. The following mixtures, in sealed tubes, were exposed to the sunlight:

TABLE I.—*Sealed tubes containing p-quinone and methyl alcohol exposed to sunlight in Manila, January 11 to January 13, 1910.*

Tube No.	Duration of exposure.	Composition of mixture.	Analysis.
	Days.		
1	2	5 cc. solution	Formaldehyde.
2	2	5 cc. solution, 5 cc. water.	Formaldehyde and quinol.
3	2	5 cc. solution, 10 cc. water.	Formaldehyde 8 parts in 1,000. Neutral to rosolic acid and to litmus paper.
4	2	10 cc. solution	Formaldehyde.

The formaldehyde was quantitatively determined by the ammonia method. Qualitative tests were obtained by three methods, Leach's, Hehner's, and Rimini's, upon the distillates obtained by volatilization with steam. Quinol was identified by the formation of quinhydrone and by oxidation to p-quinone. All of the tubes were not analyzed for all of the reaction products, and in the above table the results of tests which were made are recorded.

[4] *Journ. Chem. Soc. London* (1909), **95**, 35.

[5] Eder, Photochemie. Halle a. S. (1906), 357.

[6] *Ibid.*, 363.

II. THE OXIDATION OF METHYL ALCOHOL UNDER THE INFLUENCE OF A, SUNLIGHT, AND, B, HYDROGEN PEROXIDE.

INTRODUCTION.

During the study of the hydrolysis of methyl salicylate,[7] it was noted that this ester was quite prone to turn yellow when exposed to the sunlight. The isolation of the compounds formed prove to be quite difficult and necessitated a preliminary investigation of the products of hydrolysis. Formaldehyde was usually found in the reacting mixture when the hydrolysis was carried on in the sunlight, especially in the presence of acids, and since this compound could only result from the oxidation of methyl alcohol which, according to the available literature, was impossible, the first phase of the investigation concerned itself with this problem.

A. THE OXIDATION OF METHYL ALCOHOL IN THE PRESENCE OF OXYGEN AND SUNLIGHT.

While methyl and ethyl alcohols have been oxidized to the corresponding aldehydes by the influence of sunlight in the presence of other reacting substances or catalyzers, no aldehydes have been detected, previous to this work, when the sunlight acted in the presence of oxygen and water alone.

From the general behavior of the alcohols it is to be expected that a reaction will take place with oxygen, the governing conditions being temperature and intensity of the light.

Nef[8] has found that formaldehyde and acetaldehyde are among the products formed by the dissociation of methyl and ethyl alcohols under the influence of heat at about $600°$. Methyl alcohol dissociates and the products unite in view of the methylene hypothesis, according to the expressions

$$CH_3OH = CH_2< + H_2O = H_2C:O + H_2 = C:O + 2H_2.$$
$$CH_2< + 2H = CH_4.$$
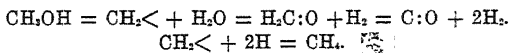
He points out[9] that the dissociation temperature of compounds may be lowered very much through the influence of agents such as light, the silent electric discharge, powdered metals, water, alkalies, or acids.

[7] Part I. The separation of salicylic acid from methyl-salicylate and the hydrolysis of the ester. *This Journal, Sec. A* (1908), 3, 101; and *Journ. Am. Chem. Soc.* (1908), 30, 1465; Part II, Solubility in water at $30°$. *This Journal, Sec. A* (1908), 3, 357; Part III. The coloration of methyl-salicylate and some allied compounds in the sunlight, by H. D. Gibbs, R. R. Williams, and D. S. Pratt. See the following article, page 79; Part IV. The saponification of methylsalicylate and methyl benzoate, by H. D. Gibbs and R. R. Williams. In press.

[8] *Ann. d. Chem. (Liebig)* (1901), 318, 195.

[9] *Ibid.,* (1897), 298, 202.

C. Neuberg[10] obtained formaldehyde and acetaldehyde by the action of sunlight on aqueous solutions of methyl and ethyl alcohols in the presence of oxygen and uranium salts, while in the absence of uranium salts no action was observed. The methods he employed for testing for formaldehyde are not stated.

Brochet[11] found that under the influence of sunlight the reaction between chlorine and methyl alcohol proceeded with explosive violence. When restrained by diluting with water, formaldehyde was formed.

With bromine he observed no reaction in the sunlight at ordinary temperatures, at 100° a slight reaction, and at from 130° to 150° an energetic one with the production of some formaldehyde.

Oechsner De Coninck[12] found that methyl and ethyl alcohols are decomposed by ferric chloride in presence of light, with the formation of formaldehyde and acetaldehyde respectively.

Benrath[13] studied the oxidation of methyl alcohol in the presence of sunlight and ferric chloride. A solution of 25 grams of sublimed ferric chloride in 90 grams of water-free methyl alcohol was decolorized after fourteen days' exposure to the sunlight. The products formed were methyl chloride, chlormethyl alcohol, hydrochloric acid, and ferrous chloride with 4 molecules of methyl alcohol in combination. When methyl alcohol in aqueous solution was employed, the hydrate $FeCl_2 \leftarrow 4H_2O$ was formed. Formaldehyde is regarded as an intermediate product, and first formed as a result of the oxidation.

Ciamician and Silber[14] have found isobutyleneglycol, ethyleneglycol, isopropyl alcohol, and formaldehyde to be the products of the action between methyl alcohol and acetone exposed to sunlight for over one year.

Beilstein[15] states that pure ethyl alcohol is unchanged in the air and that methyl alcohol is in general less oxidizable than ethyl alcohol.[16] Richardson and Fortey[17] exposed pure methyl, ethyl, propyl, and amyl alcohols to the action of sunlight, in the presence of an excess of water and of oxygen, for a period varying from a few days to six months and tested for the presence of hydrogen peroxide by means of the titanic acid reaction. Methyl alcohol showed no hydrogen peroxide and remained neutral to litmus. Ethyl alcohol "seemed to show the presence of a trace of hydrogen peroxide at the end of a few weeks," but after prolonged exposure was free from it and was neutral to litmus. N-propyl, iso-propyl, and iso-butyl alcohols gave negative results in every case while amyl alcohol showed large quantities of hydrogen peroxide and valerianic acid.

In view of the following experimental work it is not unreasonable to expect that hydrogen peroxide would not be detected even though it were the principal oxidizing agent.

[10] *Biochem. Zeit.* (1908), **13**, 305.

[11] *Compt. rend. Acad. sci.* (1895), **121**, 130.

[12] *Compt. rend. Acad. sci.* (1900), **131**, 275.

[13] *Journ. f. prakt. Chem.* (1905), II, **72**, 220; and *Ann. d. Chem. (Liebig)* (1911), **382**, 222.

[14] *Ber. d. deutschen chem. Ges.* (1911), **44**, 1280.

[15] Handbuch Org. Chem. (1893), **1**, 223.

[16] *Ibid.,* Ergn. (1907), **1**, 71; Lobry de Brun, *Ber. d. deutschen chem. Ges.* (1893), **26**, 272.

[17] *Journ. Chem. Soc. London* (1896), **69**, 1351.

If we accept the experimental work of A. Richardson upon amyl alcohol [18] and ether,[19] the presence of water and, therefore, hydrogen peroxide is not necessary for the oxidation of these compounds in presence of sunlight. In the first case the amyl alcohol was dried over sodium, sealed in a tube which was later broken in a large tube through which oxygen, dried over phosphorus pentoxide, previously had been passed. In the second case the ether was purified and dried by means of phosphorus pentoxide in an apparatus especially designed for the purpose, sealed in tubes which were broken in an atmosphere of dry oxygen, and exposed to the sunlight. In all cases hydrogen peroxide was found, and Richardson believed that it was formed in the place of water which would normally be an oxidation product. The reaction with ether he gives as

$$2(C_2H_5)_2O + 5O_2 = 4CH_3.COOH + 2H_2O_2.$$
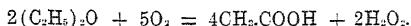
With artificial light of short wave length no difficulty has been experienced in decomposing methyl alcohol either alone or in the presence of oxygen, and formaldehyde has been identified as one of the products of the reaction.

H. Thiele [20] found that air and methyl alcohol contracted slightly in volume on exposure to ultra-violet light of the quartz mercury lamp and he states that the alcohol is probably oxidized.

Berthelot and Gaudechon [21] decomposed methyl and ethyl alcohol by means of the light of the quartz mercury lamp and found that the corresponding aldehyde and hydrogen resulted. The reaction with methyl alcohol is represented as follows:

$$CH_3.OH \rightarrow H_2C:O + H_2.$$
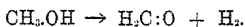
This is the reaction produced by Orlov by means of a catalyzer without the aid of external energy.

The mechanism of the oxidation of methyl alcohol by light and oxygen is explained by the presence of hydrogen peroxide. In the absence of water, and consequently hydrogen peroxide, the minute dissociation of the alcohol, perhaps according to the methylane idea, is an interesting possibility.

EXPERIMENTAL. PREPARATION OF METHYL ALCOHOL.

Methyl alcohol was purified by four different methods and, wherever samples are employed in the following paper, the method of purification will be referred to by number.

First method.—Pure benzoic acid from toluene was converted into methyl benzoate, employing Kahlbaum's methyl alcohol and pure sulphuric acid.

[18] *Journ. Chem. Soc. London* (1896), **69**, 1349.

[19] *Ibid.*, 1352.

[20] *Ber. d. deutschen chem. Ges.* (1907), **40**, 4916.

[21] *Compt. rend. Acad. sci.* (1911), **153**, 383.

The methyl benzoate was dried over fused calcium chloride and purified by distillation. About 2 kilograms of a constant boiling product were obtained.

This was hydrolyzed in 500-gram lots with fused potassium hydroxide and the methyl alcohol distilled. The distillate was fractioned until a portion of fairly constant boiling point was obtained.

The final drying was accomplished by means of metallic calcium.[22] The methyl alcohol and calcium were heated on a water bath with reflux condenser for a number of hours and distilled. This operation was repeated with fresh calcium four times.

Second method.—Pure methyl oxalate was prepared from the same alcohol, Kahlbaum's, and pure, dried oxalic acid. The purified crystals were hydrolyzed, and the methyl alcohol obtained and dried by the same procedure as that employed in the first method.

Third method.—One liter of methyl alcohol (Kahlbaum) was treated with 10 grams of calcium and allowed to stand about ten days. It was then distilled with a fractioning column and the distillate collected in 5 fractions of about 150 cubic centimeters each. The boiling point was constant throughout the distillation. The residue in the distilling flask was discarded. Each fraction was tested for formaldehyde by Remini's, Leach's, and Hehner's methods[23] with negative results. The middle fractions only were used.

Fourth method.—A portion of the product from the third method was further purified by treating with m-phenylenediamine hydrochloride[24] (3 grams per liter). After standing five days at 30° it was fractioned with a glass fractioning column. Only the middle fractions were employed.

No traces of formaldehyde could be discovered in any of the samples of alcohol employed in the following investigations.

EXPOSURE TO SUNLIGHT.

With one exception, all of the samples exposed to sunlight were sealed in tubes of very thin glass, the absorption spectrum of which showed that all of the short wave lengths found in sunlight, and even considerably shorter waves, were transmitted.

The preliminary experiments, performed more than two years prior to the bulk of this experimental work, showed that formaldehyde was produced in samples of the purest methyl alcohol prepared by Kahlbaum, when exposed to the sunlight in the presence of air. In the following Table II, the character of the mixtures and the length of time during which they were exposed are tabulated.

[22] Gyr, *Ber. d. deutschen chem. Ges.* (1908), 41, 4322.

[23] *Bull. U. S. Dept. Ag., Bu. Chem.* (1908), 107, (revised) 185.

[24] *Ibid.,* 96.

TABLE II.—*Mixtures of methyl alcohol, air, and water exposed to the sunlight in sealed tubes.*

Tube number.	Contents of tubes.	Exposure.	
		From—	To—
		1909.	1909.
I	1 cc. methyl alcohol, 10 cc. $\frac{N}{10}$ sulphuric acid	Aug. 10	Dec. 21
II	1 cc. methyl alcohol, 10 cc. water	Aug. 10	Dec. 21
III	4 cc. methyl alcohol, 10 cc. water	Aug. 10	Dec. 21
		1910.	1910.
IV	......do...	Jan. 12[a]	Jan. 13[b]

[a] 10 a. m.   [b] 8 a. m.

The methyl alcohol and all the reagents employed were carefully tested for formaldehyde before the tubes were sealed, with negative results. At the end of the four months' exposure, tubes numbered I, II, and III were found to contain formaldehyde. The amount was estimated at 1 to 5,000 in tube number I, less in number III, and least in number II. The tests employed, the milk and sulphuric acid method of Hehner, and the phenylhydrazine method of Rimini, both gave very strong, positive reactions.

Tube number IV, after not more than six hours' exposure to a bright sun on a day which was shown to be very actinic by the rate of decomposition of oxalic acid in presence of uranium acetate,[25] contained a small quantity of formaldehyde.

After these preliminary tests the methyl alcohol was purified as previously described and an extensive series started. This is recorded in Table III.

In general, the tubes containing the highest concentrations of alcohol showed the greatest quantities of formaldehyde; that is, dilution reduces the speed of the reaction. The presence of sulphuric acid increases the rate of oxidation.

Control tubes wrapped in tin foil and kept in the dark at room temperature failed to show the presence of formaldehyde. A control protected in the same way and kept in a steam bath at 100° gave faint tests for formaldehyde by all three methods; the amount formed, however, was so small that there could be no doubt that the sunlight was the important factor.

[25] Bacon, *This Journal, Sec. A* (1910), **5**, 285.

TABLE III.—*Mixtures of methyl alcohol, water, and air exposed to the sunlight in sealed tubes for varying lengths of time and the results of tests for formaldehyde.*

Number of tube.	Date sealed and put in sun.	Date opened.	Contents of tube.		Tests of contents for formaldehyde.			Remarks.
			Methyl alcohol.	Water.	Hehner's.	Leach's.	Rimini's.	
6	Oct. 18, 1911	Dec. 5, 1911	5 cc. 3d method	None	Good	Excellent	Good	
8	...do	...do	...do	...do	...do	Good	Excellent	
1T	...do	Oct. 31, 1911	...do	5 cc	Light		Light	
7	...do	Dec. 5, 1911	...do	None	Positive	Positive	Positive	
12	...do	Oct. 31, 1911	1 cc. 3d method	5 cc	Trace		Trace	
6F	Oct. 19, 1911	Dec. 6, 1911	5 cc. 3d method	...do	Positive	Good	Positive	Control kept in dark.
8H	Oct. 20, 1911	Dec. 5, 1911	...do	...do	Positive	Positive	...do	
7B	Nov. 6, 1911	...do	5 cc. 1st method	Conductivity water 5 cc	Good	Positive	...do	
13B	Oct. 31, 1911	...do	10 cc. 4th method	None	Strong	Strong	...do	
11B	...do	...do	...do	5 cc. conductivity H2O	Positive	Positive	...do	Not so strong tests as 13B.
7G	...do	...do	5 cc. 4th method	...do	...do		...do	Less formaldehyde than 13B or 11B.
9I	Oct. 24, 1911	...do	...do	5 cc	...do	Excellent	...do	
3C	Oct. 26, 1911	...do	...do	...do	Good	Good	Good	
11K	Dec. 2, 1911	...do	...do	...do	Positive	Positive	Faint	

A sample of methyl alcohol purified by the fourth method was mixed with an equal volume of water and exposed for two days (Nov. 2, 1911, to Nov. 4, 1911) in a flat dish covered by a quartz plate to the action of the sun's rays and then tested. A considerable amount of formaldehyde was found to be present.

The contents of a number of the tubes, and the alcohol exposed in the dish last mentioned, were tested for hydrogen peroxide by means of the titanium and the vanadium reagents, with negative results.

It is interesting to note that almost all of the above exposures were made at a season of the year which is most unfavorable for sunlight work in this locality, not only because the sun is so far in the south but also because of the large number of cloudy days.

It is probable that little or no formic acid results from the oxidation, for a number of solutions tested showed no acidity with blue litmus paper.

B. THE OXIDATION OF METHYL ALCOHOL BY HYDROGEN PEROXIDE.

It is not recognized in the literature that methyl alcohol and hydrogen peroxide react with each other.

Lobry de Brun[25] found that methyl alcohol was oxidized to formaldehyde by chlorine or bromine. The reaction rate depends upon the temperature and is much more rapid in the case of ethyl alcohol.

Fenton and Jackson,[27] as a result of their experiments, state that all the monohydric alcohols examined, namely methyl, ethyl, propyl, isopropyl, and amyl alcohols, were unaffected by hydrogen peroxide either in the presence or absence of ferrous sulphate, while in the case of the polyhydric alcohols, hydrogen peroxide was practically without effect in the absence of ferrous iron and active in its presence. Their solutions were tested with Fehling's solution and Schiff's rosaniline reagent with negative results.

In connection with the oxidation of ethyl alcohol it is interesting to note the work of Chauvin[28] upon distilled beverages. He found that by treatment with hydrogen peroxide the musty taste and odor could be completely removed from brandy and rum. Among the changes produced, a remarkable increase in the aldehydes was especially noted. An increase in the aldehydes also resulted on adding hydrogen peroxide to rectified spirits.

The catalytic oxidation of methyl alcohol to formaldehyde has lately been studied by Orlov[29] and he has determined the conditions required for setting the catalyzer aglow and converting methyl alcohol into

[25] *Ber. d. deutschen chem. Ges.* (1893), 26, 272.

[27] *Journ. Chem. Soc. London* (1899), 75, 1.

[28] *Mon. Sci.* through *Chem. Abstracts* (1909), 3, 2726; (1910), 4, 949.

[29] J. Russ, *Phys. Chem. Soc.* 39, 855, through *Chem. Abstracts* (1908), 2, 263, 1692, 3346; (1909), 3, 1147.

formaldehyde without the aid of external energy. The principal reaction $CH_3OH \rightarrow HCHO + H_2$ is not reversible under the described conditions.

Since it is well known that formaldehyde is oxidized to formic acid by hydrogen peroxide, it seems at first thought, that the detection of formaldehyde, an intermediate product of the action of hydrogen peroxide on methyl alcohol, would offer some difficulties. My experience has been quite to the contrary.

According to Blank and Finkenbeiner,[30] hydrogen peroxide in alkaline solution, in the cold, acts on formaldehyde according to the equation,

$$2HCHO + 2NaOH + H_2O_2 = 2H.\ COONa + H_2 + 2H_2O.$$
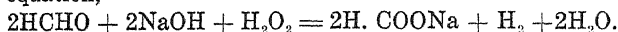
Kastle and Loevenhart[31] found that hydrogen peroxide oxidized formaldehyde to formic acid with extreme slowness at ordinary temperatures but with great velocity at the temperature of boiling water. They calculated the reaction velocities at 20°, 26°, 40°, 50°, 60°, 70°, 80°, 90°, and 98°. Light accelerated the reaction.

Lyford[32] found that formaldehyde was completely destroyed by neutral hydrogen peroxide solution at elevated temperatures, formic acid being the principal product. The latter is only intermediary. This compound is further acted on with the production of carbon dioxide, hydrogen, and water.

Loevenhart and Kastle[33] four years later state:

"1. That in the absence of formic acid the oxidation of formic aldehyde by hydrogen peroxide is greatly accelerated by finely divided platinum.

"2. That, whereas, formic aldehyde is much more easily oxidized by hydrogen peroxide alone than formic acid, the latter is about twice as readily oxidized as the former by hydrogen peroxide when platinum is present; and that when a mixture of the acid and aldehyde are present in equal quantities with spongy platinum and a quality of hydrogen peroxide sufficient to oxidize either but not both, to the next higher state of oxidation, the acid is oxidized almost to the exclusion of the aldehyde."

My experiments show that formaldehyde is formed on treating methyl alcohol with hydrogen peroxide and, even though formic acid is also formed, the formaldehyde increases as the oxidation proceeds. The temperature is an important factor in the speed of the reaction and, while I have not worked below room temperatures, I see no reason for doubting and many reasons for believing that the action proceeds at lower temperatures.

<center>EXPERIMENTAL.</center>

Two different makes of hydrogen peroxide were employed in the following work. One, from E. Merck, Darmstadt, contained

[30] *Ber. d. deutschen chem. Ges.* (1899), 31, 2979.

[31] *Journ Am. Chem. Soc.* (1899), 21, 262.

[32] *Journ. Am. Chem. Soc.* (1907), 29, 1231.

[33] *Am. Chem. Journ.* (1903), 29, 432.

a small amount of sulphuric acid and the other from Parke, Davis & Co., Detroit, contained traces of sulphuric acid and about 0.4 per cent acetanilide. No differences were observed in the effect of the two varieties. The strength of the hydrogen peroxide varied from 0.65 to 2.8 per cent.

Various concentrations of methyl alcohol, water, and hydrogen peroxide were experimented with and, at every concentration employed, reactions for formaldehyde were obtained.

Very early in the work it was observed that tests for formaldehyde could be obtained with dilute solutions when concentrated solutions failed. This was soon traced to the interference of hydrogen peroxide with both the Leach and Hehner tests for formaldehyde.[34] Rimini's test is apparently not effected by the presence of hydrogen peroxide.

The reaction between hydrogen peroxide and methyl alcohol proceeds at temperatures below 100°. I have been able to detect small amounts of formaldehyde on mixing the two liquids at room temperature and testing the mixture after about five minutes. The Rimini reaction is always positive under such conditions, while the two milk reactions, Leach's and Hehner's, are not obtained until after the hydrogen peroxide is decomposed by a reducing agent or a catalyzer. For this purpose I have employed sodium acid sulphite, finely divided metals, and hydrogen sulphide. It is, of course, realized that catalyzers introduce a complication since by their action the oxidation may be facilitated, but in view of the fact that the Rimini reaction is positive and from the other results of this work, I believe the conclusion is justified that methyl alcohol and hydrogen peroxide react with each other to produce formaldehyde.

Kahlbaum's methyl alcohol purified as described under the third method was first employed.

Three tubes were sealed as follows:

TABLE IV.—*Showing contents of tubes sealed October 19, 1911.*

No.	Methyl alcohol.	Water.	Hydrogen peroxide.
	cc.	cc.	cc.
3	5	10	2
11	5	5	2
15	5	0	2

[34] See the following paper, p. 77, on the interference of hydrogen peroxide with the milk tests for formaldehyde.

During the process of sealing, all tubes were partially immersed in ice water and only the protruding constriction heated, in order to avoid all possibility of oxidation. These precautions were found to be especially necessary where alcohol of high concentrations was sealed in the tubes.

These three tubes were then wrapped in a cloth, put in a steam bath, and maintained at 100° for four hours. They were then cooled, opened, and tested for formaldehyde by the previously mentioned three methods. Each tube gave positive results by each method; that is, 9 positive tests were obtained.

Two tubes containing 10-cubic-centimeter portions of a mixture of 25 cubic centimeters methyl alcohol, 25 cubic centimeters of pure water, and 5 cubic centimeters of a 3 per cent solution of hydrogen peroxide were sealed in tubes and placed in a steam bath at 100°. The first tube was opened after nineteen and one-half hours and the second after forty-four and one-half hours. The acidity had increased from 0.25 cubic centimeter $\frac{N}{10}$ at the beginning to 0.80 cubic centimeter in the first tube and 1.20 cubic centimeters $\frac{N}{10}$ in the second. Both tubes gave positive tests for formaldehyde by the three methods and the second tube contained very much the greater amount.

The following mixtures were next heated to 100° for varying lengths of time.

TABLE V.—*Showing mixtures heated to 100°.*

No.	Methyl alcohol.	Water.	Hydrogen peroxide.	Heated for—
• 13 M.	5	5	0	24 hours.
2 B.	5	5	0	67 hours.
13	5	5	2	67 hours.

Tube number 13, containing the methyl alcohol and hydrogen peroxide gave very strong and conclusive tests for formaldehyde by the Leach, Hehner, and Rimini reactions. The other two gave no positive tests although in one case there was a faint color reaction which could not be taken as conclusive. Tubes numbered 13 M and 2 B were tested for hydrogen peroxide by both the vanadium and titanium reactions, with negative results.

In order to prove that impurities in the alcohol were not responsible for the action with hydrogen peroxide, the following samples were employed.

Two tubes containing 10 cubic centimeters methyl alcohol purified by the fourth method, 5 cubic centimeters conductivity water, and 1 cubic centimeter hydrogen peroxide were heated to 100°

for five and twenty-five hours respectively. Both gave tests for formaldehyde by the three methods, the tube heated for the longer time contained the larger amount. Both still contained formaldehyde.

Five cubic centimeters methyl alcohol from methyl benzoate, first method, 5 cubic centimeters conductivity water, and 1 cubic centimeter hydrogen peroxide were sealed in a tube and heated to 100° for twenty-five hours. Strong tests for formaldehyde were obtained by Leach's, Hehner's, and Rimini's reactions.

III. THE QUESTION OF THE PRODUCTION OF HYDROGEN PEROXIDE BY THE ACTION OF SUNLIGHT ON WATER AND OXYGEN.

In view of the preceding article on the oxidation of methyl alcohol by the action of oxygen in the sunlight or hydrogen peroxide in the dark, it seems of interest to study the question of the formation of hydrogen peroxide by light acting on water and oxygen alone. If hydrogen peroxide is always produced under these circumstances, even in small amounts, it is not necessary to seek further for an explanation of the oxidation of methyl alcohol in the sunlight when water is present. In the absence of water, and the evidence seems to point to the conclusion that water is not necessary,[35] other theoretical considerations must be resorted to, such as the methylene dissociation of methyl alcohol or the labile hydrogen atom, to explain the mechanism of the reaction. I believe that, when working in sealed tubes as I have done, ozone formation can be excluded.[36]

It is well known [37] that hydrogen peroxide is found in the air, in rain.

[35] See work on the decomposition of methyl alcohol by light of quartz mercury lamp (Berthelot and Gaudechon), and the decomposition of ether and amyl alcohol by sunlight (A. Richardson) previously cited.

[36] On this point see *This Journal, Sec. A* (1909), 4, 143.

[37] The references in the literature are too numerous to quote. Many are to be found in Eder, Photochemie. Halle a. S. (1906). Especial attention is called to the work of Schöne, *Ber. d. deutschen chem. Ges.* (1893), 26, 3011, and (1894), 27, 1233. Richardson, *Journ. Chem. Soc. London* (1894), 65, 453, has noted that both oxygen and light are necessary adjuncts to the formation of hydrogen peroxide in oxalic acid solution.

Bach, *Compt. rend. Acad. sci.* (1897), 124, 951, states that peroxides are formed by the slow oxidation by the air in the light or in the dark of a considerable list of substances among which may be mentioned phosphorus, sodium, methyl, ethyl, isopropyl alcohols, glycerol, formaldehyde, glucose, oxalic acid, phenol, and benzene.

Franz Fischer and Ringe, *Ber. d. deutschen chem. Ges.* (1908), 41, 945, review the question of the stability of hydrogen peroxide and prepare the compound by the union of water and oxygen under a number of different conditions.

and in snow and is the product of many oxidation and other chemical reactions which proceed with and without the influence of light.

A. Richardson[38] has found traces of hydrogen peroxide in water exposed to sunlight and larger quantities in water acidified with sulphuric acid. Exposed to rays of low refrangibility, no hydrogen peroxide was formed. Water exposed to sunlight in presence of various substances such as ether, phenol, amyl alcohol, palmitic, stearic, and oxalic acids, some of the alkaloids and urine was found to contain hydrogen peroxide. In some cases the presence of water was found not to be necessary to the hydrogen peroxide formation.

Dieudonné[39] found that water exposed to light gave a weak reaction with Schönbein's reagent and, if the ether used in the reagent was mixed with the water before the exposure, the test was more pronounced.

C. T. R. Wilson[40] has shown that sunlight has the power to produce showers or fogs when acting through a quartz window or even when a glass screen was interposed between the fog chamber and the sun. He has shown that Aitken's failure to obtain this result was probably due to two causes; namely, insufficient expansion to produce condensation on the nuclei, and failure to test immediately, since such nuclei persist never longer than a few seconds.

I will quote a few brief sentences from this highly interesting article.

"It is plain, therefore, that sunlight, unlike the light from the other sources tried, contains nucleus-producing rays which can penetrate glass."

"The experiments described leave little room for doubt that pure oxygen and water vapour alone are sufficient to enable a cloud to be produced under the influence of ultra-violet light."

"In hydrogen, fogs could not be obtained under the influence of ultra-violet light without expansion."

"The view is here taken then, that under the action of the ultra-violet light small drops of water combine with the oxygen in contact with them, and in consequence of the lowering of the equilibrium vapour pressure by the dissolved H_2O_2 they are able to grow, when similar drops of pure water would evaporate."

"The absence of any effect of this kind in moist hydrogen is in agreement with the view that the growth of the drops in air or oxygen is due to the formation of hydrogen peroxide."

D'Arcy[41] has shown that hydrogen peroxide is decomposed by sunlight, and he obtained values which indicated that the days on which the radiation is most effective in decomposing hydrogen peroxide are also days on which the discharging of electrification is most pronounced.

He states:

"If the origin of the positive and negative ions in the air is due to the

[38] *Chem. News* (1889), 60, 255; *Journ. Chem. Soc. London* (1891), 59, 51; (1893), 63, 1109; (1894), 65, 450; (1896), 69, 1349 and 1352.

[39] *Arb. a. d. kais. Gsndhtamte*, A. 9, 537, through *Chem. Centralbl.* (1894), (2), 870. Also quoted by H. Thiele, *Ztschr. f. ang. Chem.* (1909), 22, 2480.

[40] *Phil. Trans. Roy. Soc. London.* (1899–1900), 192–A, 430.

[41] *Phil. Mag.* (1902), VI, 3, 42.

decomposition of H_2O_2—this substance being itself formed by the interaction of water and free atmospheric oxygen—it would seem that the phenomena of atmospheric electricity may be traced to the action of plants, if the view is correct that the free oxygen of the atmosphere is to be attributed to the action of plants."

"These experiments possibly raise the question whether some of the experiments which have been described on the action of light, in discharging negative electrification may not be due to a moisture-film containing some H_2O_2 being constantly formed and decomposed."

H. Thiele [42] found that hydrogen peroxide was formed by the exposure of water and ferrous sulphate to the rays of the quartz mercury light, and later [43] that water and air gave the Schönbein reaction for hydrogen peroxide after one-half hour exposure to the light of the Heraeus quartz mercury lamp and also reduced the concentration of hydrogen peroxide in water from 3 per cent to 0.0017 per cent in two and one-half hours.

It seems to be proved that the reaction between water and oxygen forming hydrogen peroxide is reversible and that the equilibrium point in light is at very low concentrations of hydrogen peroxide.

Kernbaum [44] has found that water is decomposed by the penetrating rays of radium with the formation of hydrogen and hydrogen peroxide and that the quartz mercury lamp will produce the same result, probably according to the reaction [45] $2H_2O = H_2O_2 + H_2$.

He states that this reaction may account for the sterilization [46] of water by means of the ultra-violet light and also for the presence of hydrogen peroxide in rain and snow which is more marked in the day than at night.

He is not correct in his ideas regarding bacteria, which by the way have been advanced by prior writers, for their destruction is not due to hydrogen peroxide formed by the ultra-violet light.

Cernovodeanu and Henri [47] obtained 0.5 milligram of hydrogen peroxide per liter on exposure of distilled water for thirty minutes, at a distance of 30 centimeters, to the light of a Westinghouse Cooper Hewitt lamp of 220 volts.

Courmont, Nogier, and Rochaix [48] could find no hydrogen peroxide after a twenty-minute exposure to the ultra-violet rays.

Chlopin [49] found that moist air exposed to the ultra-violet rays forms hydrogen peroxide, ozone, and nitrogen pentoxide.

[42] *Ber. d. deutschen chem. Ges.* (1907), 40, 4914.

[43] *Ztschr. f. ang. Chem.* (1909), 22, 2472.

[44] *Compt. rend. Acad. sci.* (1909), 148, 705.

[45] *Ibid.* (1910), 149, 273.

[46] H. Thiele and Wolf, *Arch. f. Hyg.* (1907), 60, 29. Courmont, Nogier and Rochaix, *Compt. rend. Acad. sci.* (1910), 150, 1453. Cernovodeanu and Henri, *Compt. rend. Acad. sci.* (1910), 149, 365 and others.

[47] *Compt. rend. Acad. sci.* (1910), 150, 52.

[48] *Ibid.,* 1433.

[49] *Ztschr. f. ang. Chem.* (1911), 71, 198.

Tian[50] continued the investigations of Kernbaum and found that ultra-violet mercury light, principally the wave lengths 184.6, 184.8, and 185.1 $\mu\mu$, and the waves 185.4, 185.7, and 186.2 $\mu\mu$ of the aluminum spark, decompose water into hydrogen and hydrogen peroxide. After equilibrium is established, $2H_2O \rightleftarrows H_2O_2 + H_2$, pure electrolytic gas should be evolved.

EXPERIMENTAL.

For the detection of hydrogen peroxide I have employed the titanic acid[51] and vanadic acid[52] tests, the Schöenbein[53] reaction, and Bach's[54] reagent. With dilute solutions of hydrogen peroxide I have found that, after the limits of the sensibility of the titanic and vanadic acid solutions were passed, Bach's reagent continued to show positive results.

Bach[55] has employed this reagent for the detection of hydrogen peroxide in plants. Cho[56] does not consider it to be reliable for the purpose, for he believes that other compounds in plants will produce a coloration with the reagent.

It does not seem that this criticism can apply to the cases where I have employed the test for the reason that no other known reacting substances could have been present.

Experiment I.—Three dishes containing the following mixtures were covered with quartz plates, placed in the sunlight for one day, and then examined for hydrogen peroxide.

I. Conductivity water 25 cubic centimeters; $\frac{N}{10}$ sulphuric acid 5 cubic centimeters.

II. Conductivity water 25 cubic centimeters.

III. Conductivity water 25 cubic centimeters; 1 gram sodium chloride.

The titanium reagent showed no visible reaction, while Bach's reagent gave a positive but faint test with all three solutions.

Experiment II.—The air in a tube (fig. 1), open at both ends and about one-third filled with conductivity water, was displaced with pure oxygen and the tube sealed and put in the

[50] *Compt. rend. Acad. sci.* (1911), 152, 1012, 1483.

[51] Schönn, *Dingler's Polytech. Journ.* (1873), 210, 286.

[52] Arnold and Mentzel, *Ztschr. f. Untersuch. d. Nahrungs-u. Genussmittel* (1903), 6, 305.

[53] *Journ. f. prakt. Chem.* (1860), 79, 286.

[54] *Compt. rend. Acad. sci.* (1894), 119, 1218.

[55] The reagent consists of 0.03 gram potassium dichromate and 5 drops of aniline dissolved in 1 liter of water. Five cubic centimeters of the reagent are mixed with 5 cubic centimeters of the substance to be tested and 1 drop of a 5 per cent solution of oxalic acid is added.

[56] *Chem. Centralbl.* (1896), 7, 114.

sunlight on November 2, 1911. On December 2, 1911, a positive test for hydrogen peroxide was obtained with Bach's reagent, while another portion of the same water, which had been kept in the dark during the same period, gave no test.

Experiment III.—Ten cubic centimeters of conductivity water in a sealed tube, with air, were exposed to the sunlight for three days during the month of October, 1911, and then tested. The titanium and vanadium reagents were negative while Schönbein's reagent gave a faint test. Bach's reagent was not used.

Experiment IV.—During the month of December, 1911, four sealed tubes containing conductivity water and air were exposed to the sunlight for about one week. The only reagent which showed hydrogen peroxide in these tests was that of Bach. Samples of the same water which had been kept in the dark gave no test.

The above described experiments represent the positive results obtained in about 50 different tests. With the titanium and vanadium reagents, I have never obtained a distinctly
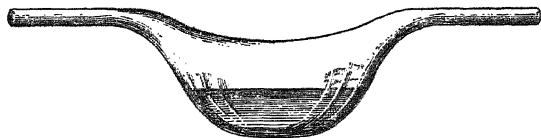
Fig. 1.—Tube used in experiment II.

positive coloration, although once the titanium reagent gave a faint indication. Schönbein's reagent will occasionally give a positive test, while Bach's reagent will give good results after skill is acquired in its manipulation. The best tests were obtained, as would naturally be expected, from water and oxygen, rather than water and atmospheric air.

In view of the fact that we are here dealing with a slow reaction, that the equilibrium is at very low concentrations of hydrogen peroxide, and, also, that the hydrogen peroxide formed during the day may possibly partially disappear at night, I am inclined to believe that the sunlight will produce the reaction and form hydrogen peroxide.

SUMMARY.

I. *P*-quinone and methyl alcohol react in the sunlight producing formaldehyde and quinol as the principal products.

II. The reaction between methyl alcohol and oxygen, producing formaldehyde as the principal product, is catalyzed by sunlight.

III. Methyl alcohol is oxydized by hydrogen peroxide. The temperature is an important factor of the speed of the reaction. Formaldehyde is the principal product.

IV. All evidence points to the conclusion that hydrogen peroxide is produced by the action of sunlight upon water and oxygen, not only in the open air but also in sealed tubes.

V. When water is present, hydrogen peroxide will thus account for various sunlight oxidations. In the absence of moisture special activities or dissociations of the molecule account for the mechanism of the reactions.

ILLUSTRATION.

THE INTERFERENCE OF HYDROGEN PEROXIDE WITH THE MILK TESTS FOR FORMALDEHYDE.

By H. D. Gibbs.[1]

(*From the Laboratory of Organic Chemistry, Bureau of Science, and the Department of Chemistry, University of the Philippines, Manila, P. I.*)

The Hehner and Leach tests both depend upon the color which formaldehyde produces with milk proteids in the presence of iron salts and strong acids, the former with sulphuric and the latter with hydrochloric.[2] These reactions are both very delicate, the latter showing the presence of formaldehyde in the milk when in the proportion of 1 to 250,000. Hehner's reaction is perhaps not so delicate, but with proper manipulation is extremely satisfactory.

I have constantly employed these reactions by mixing the solution to be tested with an equal volume of fresh cow's milk. In the climate of Manila I have observed that better results are obtained by cooling the solutions and the milk before mixing.

While studying the reaction between methyl alcohol and hydrogen peroxide[3] it was observed that both of these reactions failed absolutely in many cases where there was every reason to believe that formaldehyde was present and the Rimini reaction was positive. Mixtures of formaldehyde with milk in varying proportions from 1 to 3,300 to 1 to 200,000 were prepared and tested by both reactions. Small quantities of hydrogen peroxide were then added and the tests immediately repeated, with negative results. Instead of the characteristic violet or purple, the only colors obtained were yellow and brown.

In the dilutions employed, formaldehyde is not oxidized by the hydrogen peroxide before the test is made. The explanation of the phenomenon is to be looked for in the effect upon reactions with the proteids which produce the colored compound, or it is possible that the heat generated by the contact of the sulphuric acid in the Hehner test is responsible for the destruction of the formaldehyde by the hydrogen peroxide at the zone of contact where the characteristic color should appear. After the hydrogen peroxide is removed by reducing agents, the positive test can be obtained. In the case of Leach's test the same arguments

[1] Associate professor of chemistry, University of the Philippines.

[2] For an extensive study of this reaction, see Voisenet, *Bull. Soc. chim, Paris* (1905), **33**, 1198.

[3] See the preceding paper.

apply, for the solution must be heated almost to boiling before the color characteristic of formaldehyde appears.

Since the article was written a milk preservative called "Soldona,"[4] and consisting of formaldehyde, hydrogen peroxide, and water, has appeared upon the market. It looks as if the manufacturers are prepared to take advantage of the difficulties attending the detection of such a preservative in milk when only the Hehner or Leach tests are employed.

EXPERIMENTAL.

Solutions of formaldehyde of varying strengths, 3 to 10,000, 1 to 10,000, and 1 to 100,000, were mixed with equal quantities of milk. The concentration of the formaldehyde in the milk was then 3 to 20,000, 1 to 20,000, and 1 to 200,000 respectively. I have observed that the Hehner test is more delicate when the milk is diluted in this way than when more concentrated. Varying quantities of hydrogen peroxide were added to these solutions in the cold and, after shaking, the Hehner test was immediately applied. Some of the results are tabulated as follows:

TABLE I.—*The Hehner test for formaldehyde in presence of varying quantities of formaldehyde and hydrogen peroxide.*

Solution No.	Formaldehyde.	Hydrogen peroxide.	Character of test.
1	1 to 20,000	1 to 350	Yellow.
2	1 to 20,000	1 to 700	Brown.
3	1 to 20,000	1 to 3,000	Characteristic formaldehyde.
4	1 to 20,000	2 to 3,000	Reddish purple. Not quite characteristic.
5	1 to 20,000	3 to 3,000	Red brown. Not characteristic.
6	1 to 20,000	none	Characteristic.
7	1 to 200,000	none	Characteristic.
8	1 to 200,000	1 to 3,000	Red brown. Not characteristic.
9	1 to 200,000	2 to 3,000	Brown.
10	1 to 200,000	3 to 3,000	Yellow brown.
11	1 to 200,000	4 to 3,000	Yellow.
12	1 to 200,000	5 to 3,000	Light yellow.

In order to show that the failure of the test is not entirely due to the reaction between hydrogen peroxide and formaldehyde before the test is applied, some of the above mixtures, which produced the brown and yellow shades which are not characteristic, were treated with sodium hydrogen sulphite and sulphur dioxide and then immediately tested, with positive results. Other mixtures containing larger excesses of hydrogen peroxide, treated in the same way, gave positive results.

[4] Oskar V. Sobbe, *Chem. Ztg.* (1911), **35**, 1344.

METHYL SALICYLATE III. THE COLORATION OF METHYL SALICYLATE AND SOME ALLIED COMPOUNDS IN THE SUNLIGHT.

By H. D. Gibbs,[1] R. R. Williams, and D. S. Pratt.

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

Quite accidentally, during the investigations of methyl salicylate by one of us, the details of which have appeared in other papers[2] relating principally to the hydrolysis of this ester, it was observed that it turned yellow in the sunlight while the corresponding ester of benzoic acid remained colorless. Very early in the work, a preliminary hydrolysis experiment was so placed that the direct sunlight fell upon the solutions, producing the color in the methyl salicylate in a few hours.

Since the literature concerning the coloration in the light of a simpler compound, phenol, was so misleading, this substance was first investigated and the cause of the phenomenon found to be the oxidation of the phenol to quinone.[3]

It was at once suspected that the cause of the coloration of methyl salicylate might also be oxidation to a quinone, in fact, since salicylic acid splits off carbon dioxide under some circumstances so easily, the coloration might be due to p-quinone itself through the oxidation of the phenol formed. This phase of the question was eliminated by the investigation of the splitting off

[1] Associate professor of chemistry, University of the Philippines.

[2] Part I. The separation of salicylic acid from methyl salicylate and the hydrolysis of the ester. *This Journal, Sec. A* (1908), **3**, 101, and *Journ. Am. Chem. Soc.* (1908), 30, 1465; Part II. Solubility in water at 30°. *This Journal, Sec. A* (1908) **3**, 357; Part IV. The saponification of methyl salicylate and methyl benzoate, by H. D. Gibbs and R. R. Williams, will follow.

[3] The compounds which cause the red color in phenol. *This Journal, Sec. A* (1908), **3**, 361; the oxidation of phenol; the effect of some forms of light and active oxygen upon phenol and anisole. *Ibid.* (1909), 4, 133.

of carbon dioxide by methyl salicylate, described later in Part IV.[4] This work proved that no carbon dioxide was separated from methyl salicylate in acid solution, even at boiling temperature, while, during the hydrolysis in alkaline solution, small quantities of carbon dioxide were split off, but these were negligible in the work at hand.

The next investigation concerned itself with the possible formation of colored compounds of the nature of formaldehyde condensation products, since it was shown that the methyl alcohol, formed by the hydrolysis of the ester in acid or alkaline solution, was partially oxidized to formaldehyde[5] and it is well known that aldehydes condense with phenols and quinones forming a variety of colored compounds usually described as yellow or red.

While it is possible that small quantities of aldehyde-phenol, or -quinone, condensation products are formed after long exposure to the action of light, the first colored compounds formed and the principal cause of the coloration is not traceable to reactions of this nature. The fact that a light yellow color is produced in tubes containing only methyl salicylate, after an exposure of one hour to the sunlight, is proof of this statement. Even though traces of water might be present, the hydrolysis, producing methyl alcohol, would not have progressed sufficiently to permit of the formation of any quantities of formaldehyde which need be considered in this connection. Moreover, an inspection of the results obtained with the tubes described in Tables V and VI will show that the presence of any considerable amounts of formaldehyde will delay the color formation and reduce its intensity, probably because formaldehyde itself is more easily oxidized than methyl salicylate.[6] Furthermore, both salicylic acid and its methyl ester are oxidized with the formation of yellow or red compounds (depending upon the conditions) by hydrogen peroxide, the latter more easily than the former, the possibility of formaldehyde condensation products being the principal cause of the color is again excluded.

The coloration of methyl salicylate requires the presence of oxygen and light, or an oxidizing agent in the dark. In the

[4] To follow.

[5] The oxidation of methyl alcohol under the influence of, (a) sunlight, and, (b) hydrogen peroxide. See preceding paper, page 57.

[6] Eder, Photochemie. Halle a. S. (1906), 350. The oxidation of formaldehyde to formic acid can be brought about and the rate increased by sunlight.

light, water, alkalies, or acids are not necessary, but the coloration will take place in the presence of these substances. In neutral or acid solutions the color formed is a beautiful golden yellow, the substance formed being soluble in the methyl salicylate layer and not in the aqueous one. In alkaline solution the color is for the greater part to be found in the aqueous layer, which becomes dirty brown. This is evidently the result of secondary reactions and decompositions.

While the colored compound has not been isolated from solutions of methyl salicylate in a condition of purity which will permit of its positive identification, the evidence, deduced from its behavior and from similar compounds prepared by oxidations of methyl salicylate and related compounds, is strongly in favor of the view that the principal and initial colored compound formed is the methyl ester of quinone carboxylic acid,

$COO.CH_3$. While it is true that this compound is not

described in the literature and Nef's[7] attempts to prepare it were failures, our efforts, though not completely successful, very strongly indicate that the compound is easily formed in a variety of ways. The preparation of the mono-oxime has been successful.

Since it can not be doubted that the coloration is due to oxidation, with the formation of quinone derivatives, it becomes of interest to discuss the mechanism of the reactions. In the presence of water, or aqueous solutions, the formation of hydrogen peroxide[8] will account for all of the phenomena involved. Reasoning from the analogous behavior of phenol,[9] the oxidation of which has been proved to be independent of the presence of water, and also from the following considerations, the hydrogen peroxide assumption does not seem at all necessary, at least in the initial stages of the oxidation. Moreover, the rate of formation of the yellow color seems to be as rapid in the case of pure methyl salicylate as when considerable quantities of water are present.

The phenolic hydrogen is labile in all the free phenols which have been observed, and the absorption band heading about 277 $\mu\mu$ is characteristic

[7] *Ber. d. deutschen chem. Ges.* (1885), 18, 3499.

[8] The question of the production of hydrogen peroxide by the action of sunlight on water and oxygen. See preceding paper, page 69.

[9] *Loc. cit.*

of this form of tautomerism.[10] The exact coincidence of the bands in
different compounds, characteristic of this condition, is not material since
their position may be altered by the character of adjacent atoms or
groups. An increase in the mass of the molecule causes the oscillation
frequency to decrease and the band is shifted toward the red. Thus, the
nitrogen atom of aniline and the carboxyl group of the hydroxybenzoic
acids shift this band, and an important characteristic in its identification
is the shifting toward the red which is produced in the presence of
akalies.

The spectrum of benzoic acid[11] shows only general absorption, o- and
m-hydroxy benzoic acids[12] give a strong absorption band heading about
300 $\mu\mu$ while the para compound shows no corresponding band. The three
cresols show the characteristic band heading about 275 $\mu\mu$ and the three
dihydroxy phenols also exhibit the same uniformity. The amino phenols
are tautomeric in the same way as are the phenols. p-amino phenol, the
only one investigated by Baly and Eubank, has the characteristic band
heading about 300 $\mu\mu$.

That this tautomerism is present in all the phenols is supported
by their chemical behavior, in fact the greater the number of
hydroxyl groups, the greater the chemical activity. A notable
exception seems to be p-hydroxy benzoic acid. This compound,
as has been stated, shows no absorption band characteristic of
the labile hydrogen, and the hydroxyl group in the para position
behaves like a positive radicle decreasing the hydrogen ioniza-
tion of benzoic acid.[13]

Baly and Eubank[14] point out that the internal motions of the benzene
ring are less disturbed by the substitution of two groups in the para
position than in either the ortho or the meta. In every case which they
examined, the para compounds showed strong evidence of being more
symmetrical than the other two isomers, that is, the para compounds gave
an absorption much more closely related to the parent substance benzene,
than did the ortho or meta.

The oxidation of the phenols is much more easily effected when
the hydrogen, para to the phenol group, is not fixed. This is
especially typical in the case of the three hydroxy acids, the
ortho and meta being comparatively easily effected, while the
para acid is not changed by the sunlight in presence of oxygen,
or at least the rate of reaction is so slow as to be negligible.
In the case of p-cresol, while the para oxidation is not possible,

[10] Baly and Collie, *Journ. Chem. Soc. London* (1905), **87**, 1339.
[11] Hartley and Huntington, *Phil. Trans.* (1879), **170**, 1257.
[12] Hartley, *Journ. Chem. Soc. London* (1888), **53**, 641.
[13] Derick, *Journ. Am. Chem. Soc.* (1912), **34**, 79.
[14] *Journ. Chem. Soc. London* (1905), **87**, 1355.

still the compound is colored in the light, probably due to the formation of the o-toluquinone. In this respect the behavior of this compound is different from that of p-hydroxy benzoic acid. The fixation of the labile hydrogen increases the stability of the compound and prevents the catalytic oxidation in the sunlight. Anisole and the dimethyl ethers of the dihydroxy benzenes show no labile hydrogen atom while the mono-methyl esters present this condition.[15]

Concerning the comparative rates of the reaction in sunlight, in general it can be stated that the greater the number of hydroxyl groups, the more rapid the reaction. In the di-substituted benzenes containing one hydroxyl group the meta compound is most easily oxidized, the ortho next, and the para compound has the slowest reaction rate. The hydroxyl compounds which we have investigated[16] are the three cresols, the methyl ester of para-cresol, the three hydroxy benzoic acids and their methyl, and in some cases the ethyl esters, gentisic acid [$C_6H_3.COOH$ (1) OH (2) OH (5)] and its methyl and ethyl ester.

The esters of the phenol-carboxylic acids are all more sensitive to the action of light in the presence of oxygen than are the free acids themselves. All of the compounds, of the classes mentioned, which are colored in the sunlight are also colored by hydrogen peroxide in the dark at room temperature, and at a more rapid rate at higher temperatures.

As would naturally be expected, other oxidizing agents such as dilute nitric, chromic, and persulphuric acids, ozone and oxygen liberated at the anode produce the same effect.

Concerning the products of the oxidations there is little doubt but that the first colored compound formed is in every case a quinone. Some of these quinones are transitory products and in the case of the oxidation of salicylic acid, meta hydroxy benzoic acid, and gentisic acid, the first product of the oxidation is in each of these cases the same, the p-quinone of benzoic acid.

Rakowski and Leppert[17] obtained what they presumed to be this compound by treating hydroquinone carboxylic acid with weak oxidizing agents.

[15] Baly and Eubank, Ibid., 1349.

[16] Previous papers described the investigation of phenol, anisole, and aniline. Gibbs, This Journal, Sec. A (1908), 3, 361; (1909), 4, 133; (1910), 5, 9, and 419.

[17] Ber. d. deutschen chem. Ges. (1875), 8, 788.

Brunner[18] failed to isolate the corresponding quinone from toluhydro-quinone carboxylic acid.

Nef,[19] who studied the former compound, states that it is not possible to isolate this product of the oxidation of gentisic acid or its ethyl ester. The former decomposes, on warming with ferric chloride, into quinone and carbon dioxide and the latter is difficult of oxidation and immediately decomposes. In durylhydroquinone carboxylic acid, $C_6(CH_3)_3.(OH)_2COOH$, there is a more stable condition which admits of easy oxidation to the corresponding quinone.

The oxidation of the hydroxy benzoic acids, by means of powerful oxidizing agents such as persulphuric acid or the electric current, gives complicated condensation products. Perkin and Nierstein[20] produced catellagic acid by the oxidation of p-hydroxy benzoic acid or pyrocatechuic acid with persulphuric acid, and metallagic acid from m-hydroxy benzoic acid. Perkin and Perkin[21] state that the electrolytic oxidation of p- and m-hydroxy benzoic acids gave disappointing results and they believe the persulphate method more advantageous.

Nef's statement that the ester of hydroquinone carboxylic acid is difficultly oxidizable we have found to be rather misleading. This compound colors very rapidly in the sunlight in presence of water and oxygen, and in the laboratory is easily oxidized by dilute hydrogen peroxide, amylnitrite, potassium dichromate in very dilute sulphuric acid solution cooled by ice, very dilute solutions of persulphuric acid at 0°, and by other oxidizing agents. Decomposition does not appear to take place, at least not in the initial stages of the reaction. In all cases, the quinone color appears at once.

In alkaline solutions these oxidations are usually much more rapid and accompanied by secondary reactions and decompositions which yield, in many cases, products that have never been satisfactorily identified, a condition quite characteristic of the polyhydroxy benzenes.

Ridenour[22] states that hydrogen peroxide in 2.3 per cent solutions forms with salicylic acid in presence of ammonium carbonate a Congo-red color.

Heyl[23] observes that salicylic acid in sodium hydroxide solution gives an intense red color on shaking with hydrogen peroxide, while o-phenyl

salicylic acid, $C_6H_5.C_6H_3\big\langle\begin{smallmatrix}COOH^1\\OH\end{smallmatrix}$, gives no color. He offers no explanation,

[18] *Monatsh. f. Chem.* (1881), 2, 464.

[19] *Ber. d. deutschen chem. Ges.* (1883), 18, 3499.

[20] *Journ. Chem. Soc. London* (1905), 87, 1418.

[21] *Ibid.* (1908), 93, 1196.
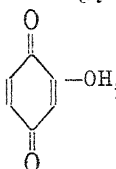
[22] *Am. Journ. Pharm.*, 71, 414, through Dammer (1903), 4, 148.

[23] *Ber. d. deutschen chem. Ges.* (1899), 31, 3035.

but from the fact that the hydrogen atom para to the hydroxyl group is fixed, this seems clear.

Salicylic acid is oxidized by potassium persulphate in alkaline solution to a product which gives gentisic acid on boiling with acids.[24]

The literature concerning the oxidation products of more complicated benzene derivatives is exceedingly confused. For example, the compara-

tively simple compound is described as varying in color from brown

to black. It has been prepared by Piria[25] by the oxidation of salicylic aldehyde in the air, by Woskressensky[26] from the oxidation of quinone in the air in caustic alkali solutions, by Büchner[27] from tannic acid, and by Sarouw[28] from the action of mono brom quinone and ammonium hydroxide. The methyl ester $C_6H_3O_2.OCH_3$ prepared by Will,[29] Bechhold,[30] and Muhlhauser[31] is evidently more easily handled and has been secured in the pure state as fine, yellow needles.

EXPERIMENTAL.

METHYL SALICYLATE AND SALICYLIC ACID.

Almost all of the tests hereinafter described were performed in sealed tubes of about 30 cubic centimeters capacity. The glass was thin and an investigation of its absorption spectrum proved that it was permeable to light of wave-length shorter than 285 $\mu\mu$ which is considerably beyond the limit of the sun's spectrum.

The first experiments, described in Table I, consisted of a series of tubes containing methyl salicylate, various aqueous solutions, and atmospheric air.

Duplicates of each mixture were prepared and treated exactly the same except that each of the duplicates was wrapped in tin

[24] Beilstein, Handb. der organ. Chem. Hamburg (1903), Erg. II. 885. D. R. P. 81, 297.

[25] *Ann. d. chem.* (Liebig) (1839), 30, 167.

[26] *Journ. f. prakt. Chem.* (1845), 34, 251.

[27] *Ann. d. Chem.* (Liebig) (1845), 53, 373.

[28] *Ibid.* (1881), 209, 107.

[29] *Ber. d. deutschen chem. Ges.* (1888), 21, 605.

[30] *Ibid.* (1889), 22, 2381.

[31] *Ann. d. Chem.* (Liebig) (1881), 207, 251.

foil to protect the solution from the light. All tubes were fastened upon the circumference of a revolving wheel, to keep the contents in constant agitation, cooled by a spray of water and kept in the sunlight for ninety-five hours. The temperature never rose above 28°, and when not in the sun, the tubes were placed in an ice box.

TABLE I.—*Sealed tubes, containing methyl salicylate and various substances with atmospheric air, placed in sunlight and in dark. Sealed on February 29, 1908, and examined March 27, 1908. In direct sunlight for ninety-five hours.*

Tube No.	Contents of tube.	Position.	Coloration.
1 5	Methyl salicylate 1 cc .... Sulphuric acid $\frac{N}{10}$ 10 cc	In sunlight .	Aqueous layer colorless. Methyl salicylate layer bright lemon yellow.
2 5	Same as last............	In dark.	Clear and colorless.
3 5	Methyl salicylate 1 cc............. Hydrochloric acid $\frac{N}{10}$ 10 cc	In sunlight .	Aqueous layer colorless. Ester layer, bright lemon yellow.
4 5	Same as last.........	In dark	Clear and colorless.
5 5	Methyl salicylate 1 cc .... Citric acid $\frac{N}{10}$ 10 cc	In sunlight .	Aqueous layer colorless. Ester layer, bright lemon yellow.
6 5	Same as last............	In dark.....	Clear and colorless.
7 5	Methyl salicylate 1 cc .... Sodium carbonate $\frac{N}{5}$ 10 cc	In sunlight .	Aqueous layer brown. Ester layer colorless.
8 5	Same as last......	In dark.....	Aqueous layer very light brown. Ester layer colorless.
9 5	Methyl salicylate 0. 5 cc	In sunlight .	Yellow. Not so bright as the tubes containing acids.

A second series of tubes, made three years later, was designed to demonstrate the effect of oxygen. The results are shown in Table II.

TABLE II.—*Methyl salicylate in the sunlight.*

Tube No.	Date sealed.	Date of final examination.	Contents of tube.	Remarks.
1 A	Mar. 9, 1911	Sept., 1911	Methyl salicylate 10 cc .... Air about 20 cc	Yellow.
2 A	....do	....do	Methyl salicylate 10 cc .... Vacuum	Colorless.
8 A	....do	....do	Methyl salicylate 10 cc .... Water 5 cc......................... Air about 15 cc	Aqueous layer colorless. Ester layer light yellow.
12 A	Mar. 11, 1911	....do	Methyl salicylate 2 cc .... Water 5 cc......................... Air about 23 cc	Aqueous layer colorless. Ester layer yellow.
13 A	....do	....do	Methyl salicylate 2 cc .... Water 5 cc......................... Hydrogen atmosphere.............	Colorless.

In addition to the tubes tabulated above, more than 50 others containing methyl salicylate with water, sulphuric acid, atmospheric air, and other substances were kept in the sunlight for periods varying from a few days to over a year. A number of these were tested for formaldehyde with positive results. When hydrolysis had proceded sufficiently, amounts as high as 1 part in 5,000 were found, the largest amounts being in the tubes containing $\frac{N}{10}$ sulphuric acid.

From the examination of these tubes (Tables I and II), the following conclusions are drawn:

In every case where oxygen was present, the methyl salicylate layer became colored in a short time. On bright days, the time required to produce a light yellow tinge was less than one hour. This color gradually deepened, the final color in some cases being a red brown. The depth of color is dependent upon the amount of oxygen available and the duration of the exposure. In the tubes containing no oxygen, namely, those with vacuum or hydrogen gas, no color was visible after several weeks of exposure to a bright sun during the dry season when the sun is at its maximum intensity. However, at the time of the final observation on August 31, 1911, a very faint yellow tinge was visible in tubes containing no acid, which we believe to be due to impurities absorbed from the glass. Faint traces of iron compounds will color methyl salicylate instantly.

When a small quantity of an acid is present which has no effect on the methyl salicylate, except to increase the rate of hydrolysis, such as $\frac{N}{10}$ sulphuric acid, the stability of the colored compound is increased, doubtless by preventing the alkalinity of the solution resulting from the absorption of impurities from the glass.

The above experiments having proved that oxidation in the sunlight is the cause of the coloration, and since it has been shown [32] that a similar oxidation may be attributed to hydrogen peroxide, the following experiments were devised to determine if hydrogen peroxide in the dark would produce similar results.

A number of tubes were sealed with methyl salicylate, hydrogen peroxide, and other substances as described in Table III, kept in the dark and examined from time to time. The hydrogen peroxide employed was a 3 per cent solution.

TABLE III.—*The effect of hydrogen peroxide upon methyl salicylate and other substances in sealed tubes in the absence of light. Room temperature about 30°.*

Tube No.	Date sealed.	Date examined.	Mixture.	Remarks.
1	June 4, 1908	July 10, 1908	Sodium carbonate $\frac{N}{10}$ 10 cc. Methyl salicylate 0.5 cc	Aqueous layer brown. Ester layer colorless. No H_2O_2.
2	do	do	Sodium carbonate $\frac{N}{10}$ 10 cc. Methyl salicylate 0.5 cc Hydrogen peroxide 2.0 cc.	Aqueous layer muddy brown. Ester layer colorless. H_2O_2 disappeared.
3	do	do	Sulphuric acid $\frac{N}{10}$ 10 cc Methyl salicylate 0.5 cc Hydrogen peroxide 2.0 cc.	Aqueous layer colorless. Ester layer yellow, H_2O_2 present.
4	do	do	Water 10 cc Methyl salicylate 0.5 cc Hydrogen peroxide 2.0 cc.	Aqueous layer colorless. Ester layer brilliant yellow. H_2O_2 present.

The yellow compound formed in the tubes, numbers 3 and 4, is reduced (decolorized) by sulphurous acid. On shaking with dilute alkalies, the color passes from the ester into the water and is intensified. This alkaline solution is also decolorized by sulphurous acid.

A number of tubes containing various amounts of hydrogen

[32] *Loc. cit.*

peroxide and methyl salicylate were sealed, wrapped in tin foil, and placed in a steam bath at 100°. The coloration appeared in a few minutes. Of a number of such tubes the following will serve as examples:

TABLE IV.—*The action of hydrogen peroxide on methyl salicylate at 100°.*

Tube No.	Contents of tube.	Remarks.
1	Methyl salicylate 2.0 cc. Hydrogen peroxide, acid with sulphuric acid, 3 per cent solution 10 cc.	Aqueous layer, colorless. Ester layer, yellow.
2	Methyl salicylate 0.5 cc. Chloroform 2.0 cc. Hydrogen peroxide same as above 10 cc.	Aqueous layer, light yellow. Chloroform layer, yellow.

These tubes were protected from the light and heated in a steam bath over night. The colored compound is reduced with the destruction of the color, by passing sulphur dioxide gas into the solution. Hydrogen peroxide and other oxidizing agents restore the color.

It is thus established that hydrogen peroxide will color methyl salicylate either in acid or alkaline solution, in a manner similar to the action of sunlight and oxygen. The temperature is an important factor of the rate of the reaction.

The following experiments were designed to show the effect of formaldehyde upon the formation of the colored compound. The tubes filled as described in Table V were wrapped in asbestos paper to protect them from the light, put in a steam bath, and examined at intervals of a few minutes until the first evidences of color appeared, and then, in order to avoid any chance of light effect, examined only at long intervals.

TABLE V.—*The effect of formaldehyde on the coloration of methyl salicylate. Temperature 100°.*

Tube No.	Contents of tube.	Remarks.
22	Methyl salicylate 2 cc. Formaldehyde 5 cc. of a 40 per cent solution	Colorless.
26	Methyl salicylate 2 cc. Hydrogen peroxide 2 cc. of a 3 per cent solution	Rapidly colored yellow in ester layer.
29	Methyl salicylate 2 cc. Hydrogen peroxide 2 cc. of a 3 per cent solution Formaldehyde 2 cc. of a 40 per cent solution	Colored yellow in ester layer, but more slowly than number 26.

111016——3

This experiment showed that the methyl salicylate in contact with hydrogen peroxide in tube number 26 colored in a few minutes and that the presence of formaldehyde in tube number 29 slowed the reaction since the hydrogen peroxide was partially used up by reacting with formaldehyde to produce formic acid. The methyl salicylate, in contact with formaldehyde in tube number 22, alone remained colorless throughout the investigation.

Experiments to demonstrate the effect of formaldehyde, methyl alcohol, and oxygen upon the coloration in sunlight are described in Table VI.

TABLE VI.—*Mixtures of methyl salicylate, formaldehyde, and alcohol in presence and absence of oxygen exposed to the sunlight in sealed tubes from March 9, 1911, to August 31, 1911.*

[Quantities are expressed in cubic centimeters.]

Tube No.	Methyl salicylate.	Formaldehyde 40 per cent solution.	Methyl alcohol.	Water.	Gas.	Remarks.
4	10	5	0	....	Air 15 cc.................	Very little color.
5	10	1	0	5	Air 18 cc.................	A little color.
16	10	0	10	....	Very little air, 0.5 cc ...	Practically no color.
7	10	0	5	5	Air 10 cc.................	Light yellow.
15	2	(a)	0	....	H.........................	No color.
17	2	0	(b)	....	H.........................	Practically no color.

ᵃ 5 cc. 10 per cent solution. ᵇ 5 cc. of 20 per cent solution.

From a study of these tubes, the conclusions are drawn that oxygen is necessary for the coloration; that formaldehyde delays the formation of color and reduces the intensity of the yellow; that methyl alcohol, when present in sufficient concentration and volume to dissolve the methyl salicylate, materially reduces the rate of the color formation, and, when present in smaller quantities so that the methyl salicylate is not completely dissolved, the amount and rate of color formation are still reduced, but not to so great an extent; and that in an atmosphere of hydrogen methyl salicylate remains colorless for weeks, the light yellow tint finally produced probably being due to impurities dissolved from the glass. The colored compound in all cases is found dissolved in the methyl salicylate layer. If formaldehyde forms any compound, under the conditions enumerated, it has no color.

Some experiments have been performed in sealed tubes in the same manner, with salicylic acid, which led to the belief that it also colors in the presence of oxygen and sunlight when dissolved in xylene or alcohol. The rate of color formation is in every case so slow that it is not certain that the reaction is not entirely due to impurities, such as iron compounds, dissolved from the glass.

TABLE VII.—*Salicylic acid and sodium salicylate in sunlight.*

Tube No.	Date sealed.	Date of final examination.	Mixture.	Remarks.
2 X	Oct. 14, 1908	Aug. 3, 1909	Salicylic acid 0.1 gram.. .. .... Sulphuric acid $\frac{N}{10}$ 10 cc	Colorless.
5 X	....do	...do	Sodium salicylate 0.1 gram ...... Water 10 cc	Brown.
7	.....do	.....do	Salicylic acid 0.1 gram .. .. Sulphuric acid $\frac{N}{10}$ 10 cc .. .. Chloroform 2 cc	Chloroform light yellow.

Salicylic acid dissolved in xylene also developed a yellow color in the sunlight. A tube containing salicylic acid 0.1 gram and $\frac{N}{10}$ sulphuric acid 10 cubic centimeters was heated for eight months on a steam bath in the dark to $100°$ with the formation of no color and no noticeable internal pressure.

The three hydroxy benzoic acids.—The meta compound is quickly acted on by the sunlight and oxygen, the ortho quite slowly if at all, and the para practically not at all.

The esters of these acids behave in the same way, but the ortho and meta are much more rapidly colored.

The three cresols.—The meta compound is colored yellow in the presence of oxygen and sunlight in about one hour and the ortho and para more slowly. The ester of *p*-cresol remains colorless.

The results obtained with these compounds in sunlight are given in Table VIII.

TABLE VIII.—*The action of sunlight upon various hydroxy benzene derivatives* [a] *in presence of air in sealed tubes. Put in sunlight on January 23, 1912. Conductivity water was employed.*

Tube No.	Contents of tube.	Condition on February 13, 1912.	Remarks.
5 C	Salicylic acid 0.2 gram........ Water 5 cc.................. Carbon tetrachloride 2 cc	Aqueous layer reddish yellow. CCl₄ layer colorless.	
6 C	Same as last, no CCl₄.........	Yellow	
13 C	M-hydroxy benzoic acid 0.2 gram. Water 5 cc .... Carbon tetrachloride 2 cc.....	Aqueous layer yellow. CCl₄ layer colorless.	
14 C	Same as last, no CCl₄.........	Yellow with red deposit......	
11 C	Ethyl ester of m-hydroxy benzoic acid 0.2 gram. Water 5 cc................. Carbon tetrachloride 2 cc.....	Aqueous layer colorless. CCl₄ yellow.	
12 C	Same as last, no CCl₄.........	Yellow with few drops of a dark-colored oil.	
15 C	Methyl ester of m-hydroxy benzoic acid 0.2 gram. Water 5 cc................. Carbon tetrachloride 2 cc.....	Water colorless.............. CCl₄ pale yellow.............. Layer of red liquid between water and CCl₄.	
16 C	Same as last, no CCl₄.........	Yellow with a few drops of dark red oil.	
9 C	P-hydroxy benzoic acid 0.2 gram. Water 5 cc................. Carbon tetrachloride 2 cc.....	Practically no color..........	
10 C	Same as last, no CCl₄.........	Practically no color..........	
7 C	Ethyl ester of p-hydroxy benzoic acid 0.2 gram. Water 5 cc................. Carbon tetrachloride 2 cc.....	Practically no color..........	
8 C	Same as last, no CCl₄.........	Colorless................	
17 C	Methyl ester of p-hydroxy benzoic acid 0.2 gram. Water 5 cc................. Carbon tetrachloride 2 cc.....	Colorless................	

[a] Many of the preparations employed were obtained from Kahlbaum, and we are greatly indebted to Mr. José I. del Rosario of this laboratory for the preparation and purification of a number of duplicate specimens of the hydroxy benzoic acids and their esters.

TABLE VII.—*The action of sunlight, etc.*—Continued.

Tube No.	Contents of tube.	Condition on February 13, 1912.	Remarks.
18 C	Same as last, no CCl4	Colorless	
3 C	Quinol carboxylic acid 0.2 gram .... Water 5 cc .... Carbon tetrachloride 2 cc.....	Aqueous layer red. .... CCl4 colorless	
4 C	Same as last, no CCl4	Red............	.
1 C	Methyl ester of quinol carboxylic acid 0.2 gram........ Water 5 cc .... Carbon tetrachloride 2 cc.....	Aqueous layer and CCl4 layer equally colored red. Deposit of dark red resinous substance	Of all the tubes tabulated here, this one colored most rapidly. Deep yellow in 10 minutes.
2 C	Same as last, no CCl4	Red. A drop of dark oil at bottom	
20 C	*O*-cresol	Light yellow............	Colored in 1 day.
50 C	*M*-cresol............	Deep yellow	First of the cresols to color. Visible in 1 hour.
51 C	*P*-cresol	Light yellow............	Colored in 1 day.
52 C	Methyl ether of *p*-cresol........	Colorless............	

The cresols in tubes numbered 20 C, 50 C, and 51 C were all pure and freshly distilled. Practically no moisture was present in the tubes.

QUINOL CARBOXYLIC ACID (GENTISIC ACID).

The esters of this compound are the most rapidly effected by sunlight and oxygen of all of the compounds studied. Preliminary studies of the oxidation of the methyl ester (colorless, crystalline compound, melting point 85°.8 corrected) for the purpose of preparing the corresponding quinone, show that the oxidation is easily effected in the cold by hydrogen peroxide, very dilute solutions of potassium dichromate and dilute sulphuric acid, very dilute solutions of potassium persulphate and dilute sulphuric acid, and other oxidizing agents. Potassium persulphate with dilute sulphuric acid seems to produce the best result although it is very difficult, in all cases, to carry the reaction to completion

without at the same time causing decomposition.   No evidence
of decomposition to para quinone has been detected in the cold.

The oxime

$$\underset{\text{NOH}}{\overset{\text{NOH}}{\parallel}} \text{COO.C}_2\text{H}_5$$

described by Jeanrenaud[33] has not

been prepared by us but the mono-oxime $C_6H_3:O,:NOH,.COOCH_3$
has been obtained in the following manner:

The calculated amount of hydroxylamine hydrochloride was added to
an alcoholic solution of the methyl ester of gentisic acid and, while heating
on the water bath, small amounts of hydrogen peroxide were added at
intervals until further additions produced no increased darkening of the
color.   After heating eight hours, the dark red solution was poured into
water causing the separation of a heavy, brownish red oil.   This was washed
with water until free from hydroxylamine, then with small amounts of ethyl
ether until practically free from unoxidized ester.   This oil is slightly
soluble in water, more soluble in ether, coloring the latter solvent a clear
dark red, and solidifies at low temperatures to an amorphous condition.

Further purification was effected by precipitation with dilute sulphuric
acid from a solution in dilute alkali, in which the oil is very soluble.
The brown flocculent product thus obtained was centrifugated, washed with
cold water to remove inorganic salts, and dried at 100°.   It was an amor-
phous, dark, chocolate-colored, almost black, powder.

The analysis was effected by the following method which has
been tested with various oximes and found satisfactory.[34]   The
$=NOH$ group is first reduced to the hydroxamic acid group by
boiling with dilute sulphuric acid and zinc dust and then the
nitrogen determined by the Kjeldahl method.

0.2231 gram substance required 11.6 cubic centimeters $\frac{N}{10}$ sulphuric acid.

	Found (per cent).	Calculated (per cent).
Nitrogen in $C_6H_3,:O,:NOH,.COOCH_3$	7.28	7.73

Considering the difficulties experienced in purifying the small
yield, the analysis is satisfactory and further establishes the
fact that the methyl ester of gentisic acid forms a quinone with-
out the loss of carbon dioxide.   The nitrogen content of an
oxime of this constitution $(C_6H_3.CH_3,:O,:NOH)$ would be 10.22
per cent, much greater than that found on analysis.

[33] *Ber. d. deutschen chem. Ges.* (1889), 22, 1283.   This compound will be
further discussed in a later article.

[34] Orndorff and Pratt, *Am. Chem. Journ.* (1912), 47, 94.

The oxidation of methyl salicylate, which should give the same compound as that obtained from the oxidation of the methyl ester of gentisic acid, has been effected by various oxidizing agents.   Rather dilute solutions of potassium dichromate and sulphuric acid in the cold seem to work well, but give poor yields. The electrolytic oxidation by means of a rapidly rotating gauze anode in a porous cell containing methyl salicylate with dilute sulphuric acid as the electrolyte [35] seems to produce the best result.   The rapidly rotating anode stirs the slightly soluble ester into an emulsion and hastens the oxidation.   The small amounts of the yellow compound which have so far been isolated behave the same as the compound obtained by the oxidation of the methyl ester of gentisic acid.   This yellow substance is decolorized by sulphurous acid and the quinone yellow is restored by oxidizing agents.   The compound is not para quinone and has every appearance of being the quinone sought.

SUMMARY.

This paper records the results of the study of the action of sunlight upon various phenolic compounds and is a continuation of the investigation of phenol already recorded.

The coloration of all the compounds investigated is due to oxidation, and requires oxygen and sunlight, or active oxidizing agents, such as ozone, hydrogen peroxide, oxygen liberated at the anode, chromic acid, persulphuric acid, etc., in the dark.

All of the members of this class of compounds, which color in the sunlight, contain the so-called labile hydrogen atom, and the behavior in the sunlight is intimately connected with the absorption band in the ultra-violet indicating enol-keto tautomerism.

The fixation of the labile hydrogen atom of the hydroxyl group and, in some cases, the fixation of the hydrogen atom, para to the hydroxyl group, is sufficient to make the compound stable in the presence of sunlight and oxygen.

The three cresols.—The meta compound colors most rapidly and the ortho and para more slowly.   The ester of *p*-cresol, the only one investigated, remains colorless in the presence of sunlight and oxygen.

The three hydroxy benzoic acids and their esters.—The meta

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[35] Hydrogen peroxide oxidation.   Richardz, *Ber. d. deutschen chem. Ges.* (1909), 42, 4674; *Ann. d. Phys. u. Chem. (Wiedemann)* (1885), 24, 183; and (1888), 31, 912.

acid colors most rapidly, the ortho only slightly, and the para not at all. The esters of the acids color more rapidly than the free acids. The para compound is the only one not effected.

Gentisic acid and its esters.—The methyl and ethyl esters of gentisic acid color most rapidly of all the compounds studied and the free acid is next in order of rapidity. The oxidation of the ester by means of other oxidizing agents has been investigated. The oxidation of the esters of gentisic acid, salicylic acid, and *m*-hydroxy benzoic acid should produce the same compound, the quinone of the ester of benzoic acid. This quinone is undoubtedly produced. It is not obtained in good yields and is difficult to purify. The mono-oxime has been prepared. This, and other considerations, point to the existence of this ester, and that carbon dioxide does not split off at once to produce para quinone as has been recorded in the literature.

We believe that the first and principal colored compound formed in every case is a quinone. Later, decompositions and condensations are apt to take place.

THE ALCOHOL INDUSTRY OF THE PHILIPPINE ISLANDS.
PART III.[1]

FERMENTED BEVERAGES WHICH ARE NOT DISTILLED.

By H. D. Gibbs[2] and F. Agcaoili.

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

WITH SPECIAL REPORTS FROM VARIOUS DISTRICTS.

By H. Otley Beyer, John M. Garvan, and Emerson Brewer Christie.

(From the Division of Ethnology, Bureau of Science, Manila, P. I.)

CONTENTS.

INTRODUCTION.

The only fermented, but not distilled, beverage manufactured on an extensive commercial scale in the Philippine Islands is beer. The usual process of cold fermentation of a mash made from rice, barley, other grains, and hops, is employed in the only brewery in the Islands, which is located in Manila. The output, now almost 4,000,000 liters annually, is steadily increasing and has already been tabulated for the past six years.[3] This is the only alcoholic beverage of this class which is taxed directly, and the annual revenue from the beer tax is over 150,000 pesos.[4] The product of this brewery is consumed by both the foreign and the better class of the native population, and in this respect differs from the other beverages described in this paper, which are consumed almost entirely by the natives.

[1] Part I. A study of some palms of commercial importance with special reference to the saps and their uses. By H. D. Gibbs. *This Journal, Sec. A* (1911), 6, 99 to 206.

Part II. Distilled liquors, their consumption and manufacture. By H. D. Gibbs and W. C. Holmes. *Ibid.* (1912), 7, 19.

[2] Associate professor of chemistry, University of the Philippines.

[3] *Loc. cit.*, p. 100.

[4] One peso Philippine currency is equal to 50 cents United States currency.

The best known of these native drinks is *tuba*, or palm wine, the fermented saps of various palm trees. The saps, after exuding from the palms, undergo spontaneous fermentation and are drunk at all stages of the action. No particular process of manufacture is necessary and, since the saps have been fully discussed in the previous parts of this article, no further mention is required.

The other beverages, made by natives in various parts of the Archipelago, have as their basis the juice of the sugar-cane, grains, principally rice, and a number of other materials of minor importance.[5] With the exception of the beverages made from palm saps and from the juice of the sugar-cane, they are manufactured by methods more or less peculiar to each locality or tribe, and are consumed locally.

BASI, A BEVERAGE MADE FROM THE JUICE OF THE SUGAR-CANE.

Basi is an alcoholic beverage made from sugar-cane and is very popular among the natives of the northern provinces of the Island of Luzon and the Batanes Islands. The name *basi, bassi, basy,* or *bashi* probably originated among the people of northern Luzon; the inhabitants of the Batanes Islands term the same beverage *palek.* It is interesting to note that the Batanes were named the Bashi Islands by Dampier[6] after the beverage, the name for which he spells *bashee.*

[5] A report has been received concerning the manufacture of a fermented beverage from job's-tears, *Coix lachryma-jobi* L., var. *ma-yuen* Staph, in the Province of Misamis; since, however, no samples of this beverage have yet been received, the account is omitted.

[6] Dampier's Voyages. London (1906), 1, 424. In the year 1687 Dampier wrote of the inhabitants: "Their common Drink is Water; as it is of all other Indians: Besides which they make a sort of Drink with the Juice of the Sugar-cane, which they boil, and put some small black sort of Berries among it. When it is well boiled, they put it into great Jars, and let it stand 3 or 4 days and work. Then it settles, and becomes clear, and is presently fit to drink. This is an excellent Liquor, and very much like English Beer, both in Colour and Taste. It is very strong, and I do believe very wholesome: For our Men, who drank briskly of it all the day of several Weeks, were frequently drunk with it, and never sick after it. The Natives brought a vast deal of it every day to those aboard and ashore: For some of our Men were ashore at work on Bashee Island; which Island they gave that Name to from their drinking this Liquor there; that being the Name which the Natives call'd this Liquor by: and as they sold it to our Men very cheap, so they did not spare to drink it as freely. And indeed from the plenty of this liquor, and their plentiful use of it, our Men call'd all these Islands, the Bashee Islands."

The same lack of ill effects following the drinking of *basi* is still testified to by travellers in northern Luzon.

Sugar-cane is cultivated for sugar in the southern and central islands of the Philippine group, while in the northern provinces of Luzon and in the Batanes Islands almost all of it is utilized in the production of *basi*. A small quantity of sugar is made by the inhabitants for their own use, but comparatively small amounts are exported. The *basi* industry is now increasing rapidly. As a matter of fact, during the last five years the amount of sugar-cane planted for this purpose has been doubled in order to meet the demand of the market.

The manufacture of this beverage is largely carried on by Ilocanos, who export it to the neighboring provinces. In Manila some of the dealers in native wines receive shipments of *basi*, in demijohns, which they bottle in old wine bottles and sell for 10 centavos the pint bottle. The indications are that the use of this beverage is spreading and increasing.

While the process of manufacture described below is simple, it is very slow for lack of proper machinery and the results are often uncertain. (Plate I.)

About 53 liters of *bennal* [7] are boiled in a *sinublan* [8] until the liquid is reduced to about 45 liters. (A mark or scratch on the kettle is indispensable to the kettle tender to insure that the remaining liquid is little more or less than 45 liters.) When ebullition begins, 0.25 square meter of the bark of the *samak* [9] tree is put in to intensify the red color, and 1 *chupa* [10] of the dried and powdered leaves of the same tree is added to coagulate the sediment or suspended solid in the liquid. While the liquid is boiling, it is stirred occasionally with a branch of *samak* and care is exercised in skimming off all of the scum [11] which floats on top of the liquid.

As soon as the contents of the kettle has reached the 45-liter mark, the fire is put out and the liquid is decanted into a *burnai* [12] and allowed to stand at least twenty-four hours, after which time it has thoroughly cooled.

One *salup* [13] of *parek* [14] is now put into the jar, which is then covered tightly with leaves of *samak* and placed under ground where it remains during the fermenting and ageing process. After two months the *basi* can be drunk, but the older it becomes the better the quality. It is considered that two years' ageing produces the necessary characteristics of a good beverage.

Basi often foams so rapidly after four or five days in the ground, due to the rapid fermentation, that scarcely 10 or 12 liters of the 45 are left. The cause of this, according to native superstition and belief, is insufficient boiling before the ferment is added; or, that the place where the sugar-cane was planted was made the rendezvous of lovers; and still a third

[7] The juice of sugar-cane (Ilocano).

[8] A large kettle containing at least 55 liters.

[9] *Macaranga tanarius* Muell.-Arg.

[10] Spanish measure of capacity equivalent to 375 cubic centimeters.

[11] *Lablab* (Ilocano).

[12] Ilocano name for an earthen jar. They are of different capacities. In this case a jar of 45 liters is required. Same as *tenaja* (Spanish).

[13] 1 salup=3 liters.

[14] A ferment composed 1 part of the dried and powdered leaves of the *samak* tree and 4 parts of the dried and powdered fruit of the same (Ilocano). [Note that this is the same word as *palek*, previously mentioned as being the local name for *basi* in the Batanes Islands.—H. O. B.]

reason, considered very probable, is that the sugar-cane was crushed in the month of March.

Jenks [15] has noted that *basi* is made by the Bontoc Igorots. He describes the process as follows:

"The Bontoc man makes his bá-si in December. He boils the expressed juice of the sugar cane about six hours, at which time he puts into it a handful of vegetable ferment obtained from a tree called 'tub-fig'.' This vegetable ferment is gathered from the tree as a flower or young fruit; it is dried and stored in the dwelling for future use. The brewed liquid is poured into a large olla, the flat-bottom variety called 'fu-o-foy" manufactured expressly for bá-si, and then is tightly covered and set away in the granary. In five days the ferment has worked sufficiently, and the beverage may be drunk. It remains good about four months, for during the fifth or sixth month it turns very acid.

"Bá-si is manufactured by the men alone. Tukukan and Titipan manufacture it to sell to other pueblos; it is sold for about half a peso per gallon. It is drunk quite a good deal during the year, though mostly on ceremonial occasions. Men frequently carry a small amount of it with them to the sementeras when they guard them against the wild hogs during the long nights. They say ít helps to keep them warm. One glass of bá-si will intoxicate a person not accustomed to drink it, though the Igorot who uses it habitually may drink two or three glasses before intoxication. Usually a man drinks only a few swallows of it at a time, and I never saw an Igorot intoxicated except during some ceremony and then not more than a dozen in several months. Women never drink bá-si."

<div align="center">EXPERIMENTAL.</div>

Three of the samples analyzed were collected by one of us (Agcaoili) in Piddig and one was secured by the Bureau of Internal Revenue, at Batak, both in the Province of Ilocos Norte. When judged by the taste, these samples were all considered very good.

The analytical methods followed were those of the Association of Official Agricultural Chemists, except in the determination of esters, aldehydes, and fusel oil. These were made by Mr. Holmes of the Bureau of Science according to the methods previously described.[16]

TABLE I.—*Analyses of basi.*

Source and age of sample.	Density.	Alcohol.	Total solids.	Ash.	Nitrogen.	Sugars (reducing).	Total acids [a] as acetic.
Sample from Piddig; age 1 year	0.9990	11.61	3.39	0.41	0.03	0.43	0.62
Sample from Piddig; age 2 years	0.9980	13.84	2.46	0.52	0.02	0.19	0.45
Sample from Piddig; age 3 years	0.9949	12.49	2.46	0.37	0.04	0.17	0.39
Sample from Batak; age 3 years	0.9906	16.24	2.29	0.54	0.16	0.18	0.42

[a] While the total acids are not acetic, this expression is merely used for the sake of comparison.

[15] *Pub. Phil. Ethnol. Surv.* (1905), 1, 144.
[16] *This Journal, Sec. A* (1910), 5, 23.

TABLE I.—*Analyses of basi*—Continued.

Source and age of sample.	Vola-tile acids as acetic.	Esters.	Higher alcohols.	Alde-hydes.	Expressed as grams per 100 liters of 100 proof spirits.			
					Vola-tile acids.	Es-ters.	High-er alco-hols.	Alde-hydes.
Sample from Piddig; age 1 year__	0.199	0.0123	0.0380	0.0018	859	53.0	165	7.8
Sample from Piddig; age 2 years_	0.082	0.0167	0.0298	0.0071	229	62.7	109	26.8
Sample from Piddig; age 3 years_	0.056	0.0280	0.0442	0.0040	223	10.4	177	16.2
Sample from Batak; age 3 years_	0.066	0.0290	0.0396	0.0443	202	89.4	122	136.4

BEVERAGES MADE FROM FERMENTED RICE.

The use of beverages fermented from rice is of ancient origin and very common among the natives of various parts of the Philippines and Malaysia. The historians of Magalhaes' expedition, which discovered the Islands in 1521, make frequent mention of their intoxicating qualities, and in 1686 Dampier[17] writes as follows of a rice beverage made by the natives of Mindanao.

"At last he told us, That he had provided a Jar of Rice-drink to be merry with us, and after that we should go with him.

"This Rice-drink is made of Rice boiled and put into a Jar, where it remains a long time steeping in Water. I know not the manner of making it, but it is very strong pleasant Drink. The Evening when the General [*war chief*] designed to be merry, he caused a Jar of this Drink to be brought into our Room, and he began to drink first himself, then afterwards his Men; so they took turns till they were all as drunk as Swine, before they suffered us to drink. After they had enough, then we drank, and they drank no more, for they will not drink after us. The General leapt about our Room a little while; but having his Load soon went to sleep."

Many other writers give accounts of the use of rice beverages, but the above is more or less typical of all.

William F. Pack, governor of the Mountain Province, Luzon, states that all of the tribes of the Igorots use a fermented rice beverage calling it by the names *tapuy* or *bubud*. He states:

"All old and a few young men among the Igorots use this liquor to excess, although when young men do, it is a matter of disgust and disgrace which no way affects the standing of the old men of a tribe, for they say that when a man becomes old he needs a certain stimulant to keep him in action."

The methods of manufacture vary greatly in different sections.

[17] Voyages. London (1906), 1, 371.

Calmette [18] states that in Saigon the rice is allowed to germinate five days in a large shallow basin and then is dried in a wooden kiln. This malted rice has a low diastatic power. The Chinese, Japanese, and Annamites make agreeable fermented beverages from rice and various aromatic plants.

The process of manufacture among some of the Igorots is as follows:

The rice is boiled and put in baskets to dry. When dry it is mixed with a small quantity of *bubud,* which is a mixture of powdered rice, or rice flour, the roots, leaves, seeds, and flowers of a plant called *anguad, lad-lad-king,* or *in-wood.* [19] The whole is then made into a pasty ball with water, dried in the sun, and powdered. Jars are half filled with this mixture and set away to ferment. The beverage can be drunk after three days. It is sometimes diluted with water to reduce its strength.

A more detailed description of the customs and process of manufacture in northern Luzon by H. Otley Beyer is appended.

At our request, two samples of *tapuy* were obtained by Governor Pack and forwarded to the Bureau of Science in sealed bottles. One was preserved by the addition of chloroform and one by formaldehyde. Both samples contained a considerable amount of suspended organic matter which settled upon standing, leaving a clear supernatent liquid. This was filtered and the filtrate analyzed.

TABLE I.—*Analyses of tapuy.*

Density and constituent.	Sample No. 1. Preserved with form-aldehyde.	Sample No. 2. Preserved with chloroform.
Density	0.9988	0.9980
Solids	2.26	3.16
Ash	0.34	0.49
Reducing sugars	none	0.34
Acidity as acetic	0.636	0.642
Alcohol	8.85	12.95
Sucrose	none	none

Jenks describes another Igorot drink as follows:

"The Bontoc man prepares another drink which is filthy, and, even they themselves say, vile smelling. It is called "sa-fu-eng'," is drunk at meals, and is prepared as follows: Cold water is first put in a jar, and into it are thrown all sorts of cooked rice, cooked camotes, cooked locusts, and cooked flesh and bones. The resulting liquid is drunk at the end of ten days, and is sour and vinegar-like. The preparation is perpetuated by

[18] *Viertelj. Fortschr. Chem. Nahrungsm.* (1894), 9, 98.
[19] *Bidens pilosa* L., Compositae, a cosmopolitan tropical weed.

adding more water and solid ingredients—it does not matter much what they are.

The odor of the sa-fu-eng' is the worst stench in Bontoc. I never closely investigated the beverage personally—but I have no reason to doubt what the Igorot says of it; but if all is true, why is it not fatal?"

REPORT ON THE USE OF A FERMENTED RICE DRINK IN NORTHERN LUZON.

By H. Otley Beyer.

So far as my information extends, this rice drink, in Luzon, is only made and used by the following tribes: Ifugao, Benguet Igorot, Lepanto Igorot, Amburayan Igorot, Itneg (or Tinggian), Bontok Igorot, Kalinga, and Iloko. The Iloko is the only Christian tribe making it, and with them its use is chiefly confined to the *barrios*.

This drink is known by different names among different tribes, those with which I am conversant being as follows: Pure Ifugao dialect, *búbûd;* Sub-Ifugao dialect, *baiyax;*[20] Benguet-Lepanto-Amburayan Igorot, *tapui,* or *tapoi;* Bontok Igorot, *tafui,* or *tafei;* and Iloko, *binadayan,* or *bóbud.*

Although it is made by all of the tribes mentioned above, it is secondary to *basi* (a drink made from sugar-cane) in most of them. In fact, the two are oftentimes mixed in such varying proportions that it is frequently impossible to tell which is the chief constituent. Among the Ifugao tribe, however, the rice drink is the principal and almost the only one in use. A very large quantity is used, and it is made in the following manner:[21]

The details of the manufacture differ slightly with different varieties of rice, the process here described being for the red rice known as *dayákôt* and covering a period of three days. The sheaves of rice are brought from the granary, threshed with mortar and pestle, and winnowed in the usual manner. The threshed rice is then placed in a large iron pan (known as a *palyuk*) and roasted over a slow fire until the germ of the rice is killed. Equal quantities of the roasted rice and water are

[20] The spelling of Ifugao words in this paper is in accordance with the phonetic alphabet adopted by me for use in transcribing the two Ifugao dialects. A copy of this alphabet will shortly be published in Section D of This Journal. The "*x*," representing the sound of "*ch*' in German *Bach*, is the only character used in this paper which might be misunderstood.

[21] For the method used by the Bontok Igorot in making this drink, see Jenks, *Pub. Phil. Ethnol. Surv.* (1905) 1, 144 to 145. Jenks' description is too brief to be wholly satisfactory, and contains several inaccuracies. The process in Bontok does not differ greatly from that in use in Ifugao.

then placed in the *palyuk* and boiled dry. The cooked rice is spread out in a rattan winnowing tray (*ligáu*), and when partially cooled is sprinkled with yeast (*binókbok*).[22] This yeast is thoroughly mixed with the rice by means of a wooden rice paddle. When this is accomplished, the surface of the rice is smoothed with the paddle, and covered with banana leaves which have been previously softened by warming over the fire. The rattan tray with its contents is then set away on a shelf in the back of the house, and the first part of the process (known as *ihá-añg*) is finished.

The above work has been accomplished in the forenoon of the first day. On the second day, the fermentation (known as *túmnôh*) begins to be visible, and has sufficiently progressed on the morning of the third day to call for the *mahaiig*, the last process of the manufacture.[23] The *mahaiig* is the removal of the fermented rice from the rattan tray, and the placing of it in the large earthenware jars called *buhis*. These jars are all of Chinese origin and are very highly prized by the people. After being filled, the mouths are tightly covered with banana leaves tied in place with bark cords. The jar is set away on the shelf, and the process is completed.[24]

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[22] This yeast is made by mixing finely ground rice with certain vegetable ingredients—the exact composition of which is a secret known only to the priests—and water. The resulting product is molded, while still wet, into little balls which later become hard and may be kept for a long time. Before using, it is pulverized to a fine white powder. It is made only by high ranking priests, and, during the process, no women or children may enter the house. The manufacture is accompanied by a certain religious ceremony. If mixed without this ceremony, it is believed that the yeast would either have no value as a ferment or would produce *búbûd* of a very inferior and even dangerous quality. People who wish to make their own *búbûd*, purchase a small quantity of the *binókbok* from a priest.

Since writing the above, I have learned some further details with regard to the manufacture of this yeast. The most important plant used is called *ónwâd*, in Ifugao, and its scientific name is *Cosmos caudatus* HBK., Compositæ. The other plants used have no value as yeast producers, and are used only for religious reasons. They are sacred plants, commonly used in many different religious ceremonies.

[23] The principal taboos on the making of *búbûd* are: It may only be made by men; and, no woman may enter the house during the *mahaiig*.

[24] The process of manufacture described in this paper is the one in ordinary daily use. However, for certain special ceremonies, when a considerable quantity of the liquor is to be made, the work is performed only by priests, and the process is much elaborated by the addition of certain religious ceremonies accompanied by curious antics on the part of the performers.

The liquid *búbúd,* or *baiyax,* begins to form in the jar within a few hours, and continues to form for the following three days. The remaining solid part (*lamóxna*) of the rice is known as *binabúdan* in the Pure Ifugao dialect, and as *lipág* in the Sub-Ifugao dialect. This solid part is eaten, after the liquid part (*dánum-na*) has been consumed, and is highly esteemed as a food.

If the *búbúd* is wanted for immediate use, its consumption begins as soon as the formation of the liquid is complete; that is, on the third day after the *mahaíig.* It is then sweet and only slightly intoxicating. However, it is usual to wait several days longer, when the liquor rapidly increases in intoxicating power. About the fifth day it is known as *nápgût,* that is, "powerful." At this period the drink is at its best, but it can be kept about ten days longer before it becomes too sour and bitter to drink.[25]

When thoroughly *nápgût,* this *búbúd* is very intoxicating, and one quart of it is sufficient to completely intoxicate any man, white or brown, except an Ifugao priest of the first rank. My observation has been that it requires less of the liquor to intoxicate the average white man than it does the average Ifugao.

Some varieties of *búbúd* ferment much more rapidly than others. These variations seem to be due almost entirely to the kind of rice used. Certain kinds of white rice will produce *nápgût* liquor in three days or less. On the whole, however, *búbúd* made from the red rice, *dayákôt,* is the best produced.

While this drink is used to a certain extent by all classes of Ifugaos, by far the greater part of it is used by priests in religious ceremonies. It is a sacred drink, and very few ceremonies are conducted without its use. All priests of the first rank, of whom there are about 150 in the Subprovince of Ifugao, are engaged in ceremonies approximately two out of every three days during the year, and probably consume about 150 liters each per year.

The drink is not ordinarily used by children, and very little

[25] When water is added to *búbúd* to increase the quantity, it is known as *nalitéñgan* and is then considered to be of distinctly inferior quality. Pulverized chili peppers (*páktiu*) are often added to *búbúd* used by priests in order to make it "tasty." This *napaktíuan* liquor is said to have a sobering and clearing effect upon the brain. It has a very sharp, biting taste, and an Ifugao is held not to be really a "man" until he can accustom himself to its use, and take it without a grimace.

111016——4

by women. The chief occasions on which they use it are cere-monial nights of general license (*líu-líua*), and at harvest feasts, etc. Some men can drink very little and avoid taking it when-ever possible. On the other hand, there are a few more or less habitual drunkards, who probably consume over 190 liters each per year. However, these are very few, as drinking out-side of religious ceremonies and special occasions is looked down upon by the great majority of the people. Habitual drunkards are frequently spoken of with contempt as being persons lacking proper self-control and sense of propriety.

An accurate estimate of the total quantity of this rice drink which is used by all of the tribes above mentioned is rather difficult to make. In the Subprovince of Ifugao the total quan-tity used is approximately 774,032 liters per year, or 6.6 liters per person. An estimate made by myself in consultation with Lieutenant-Governors Early of Bontok and Miller of Lepanto places the total quantity consumed by all the tribes at 3,096,500 liters per year.

REPORT ON DRINKS AND DRINKING AMONG THE MANDAYA, MANOBO, AND MANGGUANGAN TRIBES.

By JOHN M. GARVAN.

The following observations were made during two trading expeditions to the Upper Agusan River in 1907 to 1908, and during a trip of five months (1909 to 1910), in the interests of the Bureau of Science, to the Upper Agusan, Upper Cateel, Upper Caraga, and Upper Salug Rivers, and apply not only to these districts, but, according to trustworthy accounts, to the Tagum, Libaganon, and Hijo districts, thereby including almost in its entirety that part of Mindanao that lies east of the Central Cordillera between 7° and 8° north latitude.

There are in use in these regions seven drinks which may be classified as follows:

(1) A brew made from the expressed and fermented sugar-cane juice, called *tuba* by Mandayas and Mangguangans, and *intus* by Manobos.

(2) Honey-mead, called *báis*.

(3) A beverage made from the sap (called *tunggang*) of the sugar palm or *cabo negro*, as well as the sap of the *báhi* or fish-tail palm.

(4) The sap made to flow from sugar-cane of an especially large variety.

(5) The sap of the *nipa*, called *paug*.

(6) The sap of the coconut called *tuba sa niug*.

(7) The common native *vino*.

I will not refer to the sixth and seventh drinks above men-

tioned for the simple reason that they are sufficiently well known and, also, because their use is confined almost exclusively to coast towns and to Bisayas.

TUBA OR INTUS.

The most common and popular drink in the above-mentioned regions is a beverage called *intus* by the Manobos and *tuba* by the Mandayas and Mangguangans.

Extraction of the juice of sugar-cane.—A sufficiency of sugar-cane is cut down and brought by the female members of the family to the spot where the crushing appliance has been established. This consists of the trunk of a *bahi* or *anahao* palm tree rudely supported in such a way that by means of a small cross-piece it can be rolled back and forth over a rough-hewn board. The sugar-cane, being peeled and cut into pieces about 30 centimeters long, is placed piece by piece on the rough-hewn board and crushed by the weight of the cylindrical log rolling over it. The juice flows into bark platters or any other crude receptacles placed underneath.

The amount of juice sufficient for the exigencies of the occasion having been prepared in this way, it is brought, not usually to the house, but to a secret, shady place in its vicinity. I may here add that, for reasons to be explained later, much secrecy is observed in the preparation.

The ferment.—The next process, if it has not already been completed, is to pull up a quantity of *lankawas* (Manobo) or *pal-la*[20] (Mandaya and Mangguangan) roots and, after slicing them into thin pieces (the thinner the better), to pound them in an ordinary rice-mortar.

The cooking.—All is now ready for the fire. A *kaha* or *kiaja* (small iron caldron) quarter-spherical in shape and usually approximately 50 centimeters in diameter, or an ordinary homemade earthen pot, is set upon the fire, and in the center of it is placed a slatted bamboo cylinder (approximately 10 centimeters in diameter) around which is piled the mashed *lankawas* or *pal-la* root. As much sugar-cane juice as the cooking utensil can contain is then added and allowed to boil slowly until it acquires sufficient strength, a fact that is ascertained either by a measuring rod for gauging the quantity of liquid that has evaporated, or by the color, or by the smell, or by all three methods.

Various grades.—These three tests vary in different localities

[20] *Cordyline terminalis* Willd.

and give rise to various grades of beverages. The mountain Mandayas of Cateel, Manorigao, Caraga, and of the district well to the south of Compostela, evaporate only one-fourth of the sugar-cane juice, thereby producing a beverage of a milky color and sweetish taste that has a deleterious effect on those not accustomed to it. The Manobos (both *conquistas* and non-Christians) of the Upper Agusan, Ihauan, and Argauan districts, evaporate the liquid to one-half and produce a drink that, although milky in appearance and somewhat sweetish in taste, does not produce such unpleasant results. However, the *tuba* made by the Mandayas residing along the Agusan River to the south of the town of Moncayo, by the Mangguangans, and by the Debabaon group of Manobos in the district at the headwaters of the Salug River is prepared on a heaping fire, and boiled down rapidly until it acquires a fine chestnut color and an odor that can never be mistaken. This is a beverage that, after a fair amount of fermentation, proves palatable, wholesome, and exhilarating. After cooking, the concoction is left to ferment for a certain period of time in jars, or earthen pots, or in absence of these, in bamboo joints.

Fermentation.—The longer the period of fermentation, the finer the quality of the resulting liquor. Five days are sufficient to render it drinkable, but, as a general rule, it is left longer. *Tuba* (*intus*) that is a few months old is of a translucent, amber color, and smells strongly like rum. It is a wholesome drink, much stronger than coconut *tuba*, and not attended with the after-effects that are the result of over-indulgence in some other inebriating drinks.

The occasions for drinking are as follows: (1) Religious and social feasts, (2) the arrival of visitors, (3) the desire to make a good bargain, or to secure any other end by convivial means, and (4) the acquisition of an unusual amount of meat or fish.

Although this liquor is invariably used during religious feasts, yet neither during the feast itself nor in the preparation of the *tuba* have I ever observed any religious ceremony. It is true that when the *ligisan* or crushing appliance is set up, the fowl-waving ceremony (*kuyab*, Manobo and Mandaya) followed by the *payas* or "blood-unction" is performed. I witnessed these ceremonies in several parts of the Agusan River Valley. However, such ceremonies are customary on the erection of houses, smithies, and so forth, and bear no relation to the actual production of the drink.

During religious ceremonies, a bowlful of the brew is set out with the usual viands (meat, rice, etc.) for the *diuata* (Manobo and Mandaya deities), *tagbanua* (lord of the hills and the valleys), and other spirits.

The acquisition of an unusual amount of meat or fish is the ordinary occasion for drinking, as it affords the complement for the *tuba* (*intus*) and gives rise to the holding of a *sumsuman;* that is, the eating of meat or fish with an accompaniment of drink.

The *sumsum-an,* a practice universal throughout the Agusan Valley, the Salug Valley, and the whole Mandaya country, is a thing that appeals especially to the true Mandaya and Manobo and Mangguangan. After securing a good catch of fish, or after trapping a wild boar, he procures a supply of *tuba* and meets his guests at the appointed place, usually his little farmhouse. As soon as all are assembled, the fish or the meat is broiled on sticks of wood over the fire. When cooked, or rather scorched, the women lay it out and it is slashed to pieces, usually by the host, and apportioned with great precision as to weight, quality, number of bones, and amount of meat. During this operation a few bamboo jointfuls of *tuba* are brought from their hiding place, and a relative of the owner sits down with one under his arm while before him are set such articles as glasses and bowls, if obtainable, or, in lieu thereof, small pieces of bamboo joints, each holding about a tumblerful, and not very different in shape from German mugs without handles, which admirably fulfill the purpose. Having sliced a little exterior strip from under the mouth of his bamboo deposit to prevent loss of the liquor after pouring, the host inserts two fingers into the mouth of the bamboo and makes an opening for the *tuba,* but not so large as to give free exit to such insects as may have found a liquid grave in its sweetness. He then fills the vessels at hand, taking care to give to each an equal amount.

The host, at this point, passes the drink to those whom he wishes to honor and saying *adla* (Mandaya) or some such expression corresponding to our English "Here goes," they drink. The bowls or other vessels are returned to the distributor, and the process is repeated until all have had sufficient. In the meantime, pieces of pig or fish, sprinkled with red pepper and salt, are being sampled and friend vies with friend in giving tokens of good will. These tokens consist of huge handfuls of meat (lean, fat, bone, and gristle), well soused in salt (when on

hand) and red pepper, and are bestowed by one friend into the mouth of another. It is not good etiquette to refuse, nor should one remove the piece from one's mouth, no matter how unwieldy it may prove, for it will be one's turn to reciprocate the deed in kind.

When the turn of each to drink comes again, the bamboo tankard is taken by a friend and filled to overflowing. Remonstrances are of no avail, the draught must be despatched at once, for the tribesman loves a cheerful and a rapid drinker, and ample opportunity will occur to return the favor. This custom of reciprocating in food and drink is very characteristic of all the Agusan tribes except the Mangguangan who intensifies it by returning the favor *twice,* giving his friend two mouthfuls and two tankards for one.

Drinking during religious and social feasts.—The drinking customs are as above described, except that the beverage is set out in sacred jars,[27] if the latter are on hand, and with such an array of bowls as the host may be the proud and happy possessor of. One of these feasts (especially that of marriage) may be attended by as many as two hundred persons and lasts from three to seven days (*and nights*) so that to hear of 20 jars or 100 *sugung* or bamboo jointfuls of *tuba* being consumed on the occasion of a great festival is not strange.

The quantity of food and drink consumed, both individually and collectively, during one of these feasts, gives an idea of the hearty appetite which these primitive peoples enjoy. The average white man, I think, would be deliriously drunk and bloated before the Mandaya or Manobo would be feeling merry. It is not according to tribal customs to refuse meat and drink while the host has them to set before his guests. On occasions I have seen a tribesman rise, quietly empty his stomach, and calmly return to the fray to finish his appointed portion and wash his hands in his plate, as an evidence of that fact.

Women and children drink little, not from any religious or moral principles, but simply because they do not care for it. However, the men are inveterate drinkers and have an extraordinary capacity. No disgrace is attached to drunkeness. On the contrary, to take the allotted portion is considered a duty and a virtue. Man vies with man in holding out, and friend honors friend with plenteous offerings, while the host strives to keep all supplied to their utmost capacity.

Evil effects from drinking among the Manobos and Manda-

[27] Called in Mandaya and Mangguangan *bandi,* and in Manobo *bahandi.*

yas.—Quarrels sometimes result from these drinking bouts, but not oftener, I think, than they occur among more highly cultured people in other parts of the world. The custom of carrying weapons on all occasions where others than relatives are present has a deterrent effect, yet there are occasions where a recourse to daggers (Mandaya) or to *bolos* (Manobo and Mangguangan) terminates an argument which can not be settled by wild shouts and frantic gestures. I have witnessed a few instances of this. Once, in the Upper Manorigao (southeastern Mindanao), in the house of Bagani[28] Andaiyup, an argument began and every man jumped for his dagger. I retired from my place on the floor to the vicinity of my gun and, on seeing one man stab another in the leg with his dagger, I slipped down the notched pole. A few minutes later the host upbraided me for retreating, saying that it was only a little matter between relatives, and it was settled amicably.

On another occasion, in Compostela, I was doing the honors of my house to Bagani Tomando of the Upper Caraga. At the same time there was present a relative of a person in Manlubuan (Middle Cateel River, eastern Mindanao), who had been attacked by the Mandayas from Manorigao (a river near Caraga, eastern Mindanao), assisted by Tomando and others. As Padodo (for this was the name of the other Mandaya) waxed merry after several potations, he began to sing and made reference to the futile attack by Tomando and his companions on his relatives of Manlubuan. Tomando answered in song, and so the thing kept up until Tomando lost his patience and whipping out the ever-present dagger, would have struck his adversary down had I not seized his arm and besought him to desist. Padodo, however, was up and ready, but as Tomando's two brothers suddenly appeared on the scene, Padodo retreated and at once left the house and the town.

Mangguangan brawls and killings.—Drunken brawls and killings are more frequent among the Mangguangan than among the other peoples of the Agusan Valley. The Mangguangan, unfortunately for him, becomes quarrelsome in his cups, especially with members of the Mandaya and Manobo tribes for whom he bears no love. Pulling out his bolo he settles the argument with a deep slash and brings down on his head the blood reprisals that have exterminated his fellow tribesmen by

[28] Bagani is a title conferred on one who has a certain number of human lives to his credit and who is, accordingly, under the special influence and protection of a war god.

thousands.   During my last trip to the Upper Agusan, I visited the settlement of Sinantan, a Mangguangan headman.   My companion and guide, Kabatlao, in the heat of his cups, had an altercation with Sinantan.   As wild shouts on such occasions are no indication of ill-feeling, I paid no attention and the matter went on for several minutes in the fiercest manner till Sinantan snatched out his bolo and made a slash at Kabatlao.   Fortunately a few others and I prevented the blow from taking effect.

"BAIS" (MANDAYA AND MANGGUANGAN).

Bais, a kind of honey-mead, is made during the honey season where bees abound.   The district at the headwaters of the Caraga River is famous for its *bais*.   During my stay there I purchased honey to the quantity of about 100 liters.

Bais is made in the same way as *tuba* (*intus*).   Water is mixed in varying proportions with the honey, but a half-and-half mixture yields the strongest drink.   Fermentation for a period of five days is sufficient, but after a month or more it is said to result in a clear liquor that is as strong as native *vino*.

THE SAP OF THE SUGAR PALM.

This is called *tuba sa hidiup* or *tuhak* in the Lower Agusan, and *san* in the Upper Agusan.   It is obtained by tapping the flower spathe of the sugar palm.   This is done by bending the blossom shoot daily into a downward position.   The operation occupies about half-an-hour for some fourteen days.   The sap is collected in bamboo joints in much the same way as the well-known coconut *tuba*.

In appearance, the cabonegro *tuba* has the color of milky water.   When fresh it is rather sweet, but after a few hours it ferments and makes a drink as strong as coconut *tuba*, but a great deal more refreshing.   In certain localities the bark of a tree called *lamúd* is added to hasten fermentation.   This *tuba* becomes so sour on the third day that it is unfit for drinking purposes, but can be used for vinegar, *nipa* vinegar being in no wise comparable with it.   Should it be desired, however, to withhold fermentation for several days, a handful of native red peppers thrown in accomplishes the purpose.

A good *cabonegro* palm runs for about three months and affords daily about 14 liters of *tuba*.   Although used extensively, when obtainable, this drink is not considered by the non-Christian tribes a fit substitute during great feasts for the sugar-cane beverage described above.

A remarkable number of trees, in fact whole groves of them, are found in the vicinity of the town of Tudela, Simulao River, Agusan Valley. I think that there can hardly be less than 5,000 trees in that one locality.[29]

TUNGGANG (MANOBO AND MANDAYA).

Tunggang is the sap of the *bahi* (fish tail) palm extracted in the same way as coconut *tuba*. It is a drink little used for the reason that the taste and smell are unpleasant. However, it is not unwholesome. I never saw it used by any tribe in the Agusan Valley except the Manobos, and then only in the absence of other beverages. It was reported to me by Manobos living near the headwaters of the Maug River that the Mamanua[30] tap the *bahi* palm occasionally, but it is a custom acquired, I presume, from the Manobos with whom they intermarry, at least in the district at the headwaters of the river that empties into the Pacific Ocean at the town of Tago, eastern Mindanao.

THE SAP OF THE SUGAR-CANE.

This drink came under my observation only once, but, on inquiry, I have been informed by several Bisayas that the method is known and practised in places other than that in which it was witnessed by me.[31]

The species of sugar-cane that was used was a very large variety growing to a height of about 8 meters. It had a large, green stem and long joints, and was propped up on a dead tree.

The process of extracting the juice, as described to me, was as follows:

A little soil is placed around one of the joints a few feet above the ground. When the joint has thrown forth roots, the stem is cut below these roots and the portion of soil in which they grow. The sap then begins to trickle out slowly. I tasted the fresh sap and found it to be very similar to sugar-cane juice, but with much more of a snap to it. At the time, I did not observe the process of extraction closely and I have never had occasion to witness it since.

SAP OF THE NIPA OR SANI PALM, CALLED PU-AG.

This is used principally in seacoast settlements. It is obtained by tapping the fruit stem of the palm. The process consists

[29] [For a full account of the cabonegro or sugar palm see Part I of this paper. H. D. G.]

[30] Negritos inhabiting the Eastern Cordillera of Mindanao from Surigao to Lianga.

[31] The place referred to is a Bisaya settlement midway between the towns of Tago and La Paz, eastern Mindanao.

in shaking gently the stem every morning for a few minutes. Usually in about fourteen days the sap begins to trickle out. It ranks next to *tunggang* in the general estimation.

AMOUNT OF DRINK CONSUMED.

With regard to the amount of drink consumed, I can venture no approximate estimate. This will be readily understood as, according to the social institutions of the Manobos, Mandayas, and Mangguangans, it is considered no breach of manners to ask one's neighbor for anything of his to which you may take a fancy. A refusal on his part, unless couched in the most diplomatic terms and with all semblance of truth, might give rise to unneighborly feelings and prompt a reprisal in kind on some other occasion. For this reason it is always the best policy to conceal one's goods and chattels, especially meat, fish, and drink, until the time for dispatch has arrived. Hence drink is almost invariably kept out of sight, either by being wrapped in leaves, or deposited in the grass outside of the settlement, or by being brought to the destined place at night, for were others than the invited guests aware of the existence of drink they, too, would flock to it.

In view of these conditions it is impossible to give an estimate of the amount consumed in the districts above mentioned.

REPORT ON THE DRINKING CUSTOMS OF THE SUBANUNS.

By EMERSON B. CHRISTIE.

The following statements are based on personal observation of the Subanuns living around Sindangan Bay, Mindanao.

The Subanuns sometimes make alcoholic drinks from honey and from millet, and I have been told, but can not vouch for the truth of the statement, that they occasionally make a beverage from sugar-cane juice. The principal drink, and the only one which I have myself seen in use among them, is *gasi* or *pangasi*. This is made from rice in the following manner.

Rice is pounded, mixed with parts of certain plants, cooked, and laid aside to ferment. This is later dried, made into cakes or balls, and stored. When a Subanun wishes to make *gasi*, which may perhaps be called rice-beer, the women of his family cook some rice, spread it out on a mat, and while still warm, stir into it one or more of the above-mentioned balls in powdered form. The mass is then laid aside for a few hours until fermentation is well under way. Then the rice is put into Chinese jars, water is poured on, and the jars set aside. The

resulting liquor is drunk soon or late according to taste and circumstances. Up to a certain point, the longer the liquor is kept, the greater its intoxicating quality.

Before the brew is consumed, the owner flavors it according to his fancy by adding such vegetable ingredients as suit his palate. Among other things sometimes used for this purpose, I have seen wild ginger and small red peppers.

On none of the several dozen occasions during which I have seen Subanuns drink *gasi*, have I seen glasses used. This is not due to an absence of these articles. Pigafetta, the chronicler of the first journey around the world, and the first European to write observations on the Philippines, gives the following account of the manner of drinking of the King of Cebú:

"When we reached the city we found the king surrounded by many people. He had four jars of palm wine in front of him covered with sweet-smelling herbs and arranged with four small reeds in each jar by means of which he drank. The king had us drink through those slender reeds."

This is still the way in which the Subanuns drink. Before the jars are served there usually is made an arrangement of little cross-sticks or stems to keep the reeds steady. It is also common to cover the liquor with "sweet-smelling herbs." The guest of honor sucks out of the same jar as the host. (Plate III.) It is common, especially at feasts, for those drinking out of the same jar to enter into friendly rivalry. For this reason they drink one at a time, and after each drink, water is poured in to fill up the jar. This water is poured into the jars with small cups sometimes of brass and sometimes of coconut shell. The cups have each a hole in the center of the bottom. This hole is stopped by the finger when the water is taken up. To pour the water into the jar, the finger is removed. Account is kept of the number of cupfuls of water necessary to replace the amount drunk by each one. Of course the drink becomes more and more diluted as the process continues, but the operations are transferred to a fresh jar before the drink becomes too weak. As the drinkers proceed, they become less formal, the turban is allowed to fall off, the long hair, hitherto confined, falls down on the back, a slight flush appears under the brown skins, and the drinkers frequently break out into verse and song. The verse is often improvised, and dilates on such themes as the pleasure of the beer jar or the liberality of the host, a liberality which the guest protests makes him ashamed because of his inability ever to repay it. Traditional verses also float up in the consciousness of the drinkers and are shouted, to the delight of the

company. During the drinking the big gongs of the house are
usually beaten with a will for many hours at a time. The
younger men, after drinking a while, sometimes jump up and
dance. The dance is sometimes a *pas seul*, sometimes a dance
with a woman partner, whom however the man does not touch,
and sometimes it consists in joining a ring of men and women
who hold hands and leap rhythmically around a sort of Maypole
in the middle of a special dancing platform.

Drinking plays a very important part in Subanun social life.
Gasi is usually offered to a visitor of rank, whether a stranger
or not. It would, of course, be considered exceedingly rude for
the latter to refuse to drink. At feasts drink is considered as
essential as food.

These are usually given by a chief or leading man just after a
good harvest, or in honor of the dead, or in order to fulfill a vow
made to certain spirits for recovery from sickness. At such
times the amount of *gasi* consumed is often very large. I have
seen over three hundred Subanuns, at a feast, who drank *gasi*
liberally day and night for four consecutive days. I have also
seen a house with over a dozen Subanuns lying on the floor in
the daytime, sleeping off the effects of drink.

It is a common precaution at Subanun feasts for the weapons
of the guests to be delivered to the representatives of the host
before the drinking begins. This is to avoid casualities when
the men are in their cups. Before the drinking begins an
influential man designated by the host usually ties a number of
knots in various pieces of rattan attached to the wall in a con-
spicuous place, each knot representing a certain unit of value,
such as, gongs, brass cannon, or pieces of cloth. He then shouts
to the assembled company that the knots represent the amount
of the fines which will be imposed on any man who commits
during the feast certain offenses which are specified; such as
quarrelling, blows, stepping on people, and liberties taken with
the women.

In point of fact, Subanuns make allowances for the conditions
of men under the influence of drink, and small offenses are
readily condoned, but any serious injury committed under
alcoholic influence is punished, and any improper advances to
women. If I may believe what I was told on the subject, the
man offering the drink is punished as well as the immediate
culprit.

It is usual at Subanun feasts for the guests to bring their
wives and children, who eat and sleep in the host's house like
the men. Women and children are free to drink, but do not

indulge so deeply as the men. As a rule, women and children do not drink with the men, but a man sometimes invites a woman or child to drink with him, in which case the invitation is usually accepted.

Drink is offered not only to men, but to souls of the dead and to various classes of spirits. It is usual at feasts to offer little jars of drink to spirits whom it is desired to conciliate, as well as food, betel-nut, and cigarettes. The drink is placed on or beneath the altar or the image, and the spirits are formally invited by a medicine man to partake. Even apart from feasts, when a favor, for example, such as the cure of a sick man, is requested from the spirits, drink is usually a necessary part of the offering.

It is, of course, impossible to give any figures as to the extent of drinking among the Subanuns. Certain facts, however, are patent to direct observation. Drinking among these people is not a daily habit. I have never met any Subanuns who could be called drunkards. Most Subanuns drink freely, but only on certain occasions. These occasions do not come very often. In a given district half a dozen important feasts may occur in a year if the crops have been good. Aside from these more important feasts, each of which may last five or six days, characterized by free indulgence in *gasi*, lesser occasions for drinking, such as religious ceremonies, marriage, or the entertainment of guests, occur from time to time throughout the year, but not often enough to tempt the people into drinking enough to do themselves serious harm. Drinking is greatly enjoyed by the Subanun, who by means of it is lifted for a short time to a plane of existence more interesting than that of his colorless daily life. Whether he would abuse this means of escape from the flatness of existence if he had the means, I do not know. It is only a small number of chief men who would have the necessary surplus of rice to do so if they wished, and among them I have not noted habitual drunkenness.

On Sindangan Bay, I have never seen Subanuns drinking any but home-made liquor. The only instance in which I have observed a Subanun using imported intoxicants was on Duman-kilas Bay, where a leading chief once showed me a few bottles of gin and *anisado* of inferior quality from Manila. I am inclined to think that so long as the Subanuns confine their indulgence in drinking to an occasional social jar of *gasi* with visitors and to drinking bouts a few times a year at their feasts, they are not in danger of injuring themselves seriously with alcohol.

ILLUSTRATIONS.

PLATE I.

Fig. 1. Basi mill; general view showing cane crusher, boiling works, and in the foreground two *tinajas* of basi placed in the ground to ferment. Near Agoó, Union Province. (From the photograph collection of Dean C. Worcester.)

2. Boiling works of *basi* mill. Near Aggó, Union Province. (From the photograph collection of Dean C. Worcester.)

PLATE II.

Fig. 1. Sugar-cane mill (*dadapilan* Ilocano) in action. The juice, as it runs from the crusher, is used for the manufacture of *basi*. Piddig, Ilokos Norte. (Photograph by Agcaoili).

2. Cane crusher near Agoó, Union Province. (From the photograph collection of Dean C. Worcester.)

PLATE III.

Subanuns drinking rice beer from jar.

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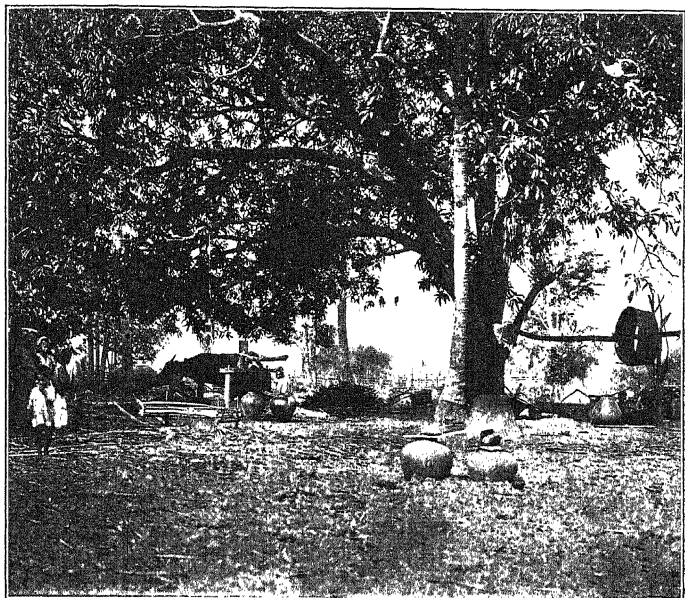
Fig. 1.   General view of basi mill.

Fig. 2.   Boiling works of basi mill.
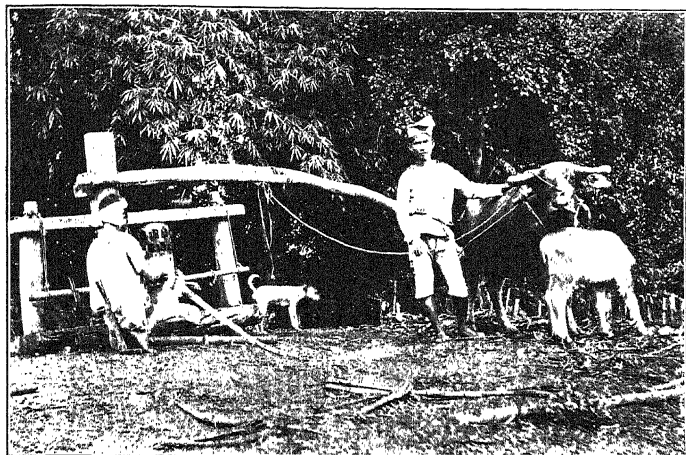
PLATE I.

Fig. 1.   Sugar-cane mill in action.
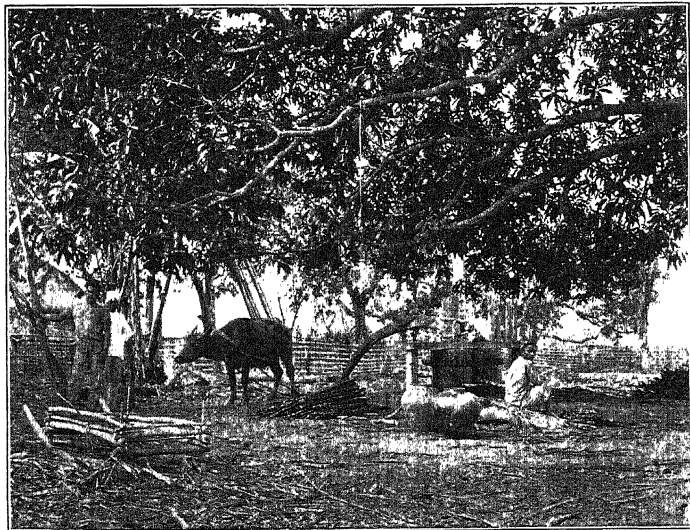
Fig. 2.   Cane crusher near Agoo, Union Province.
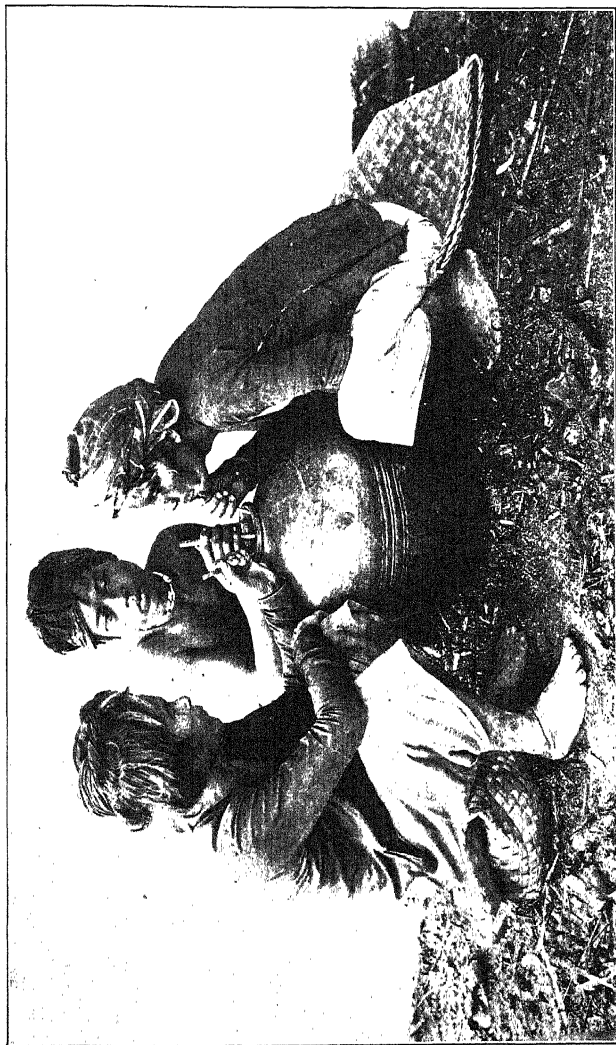
PLATE II.

Subanuns drinking rice beer from jar.

PLATE III.

EDITORIAL.

BAMBOO FOR PAPER PULP IN BATAAN PROVINCE, LUZON.

Richmond[1] has estimated the cost of bamboo pulp production in Bataan Province, Luzon, and says:

"I can state positively that there are a number of areas of bamboo of uniform stand within 5 kilometers of the seacoast, any one of which would supply a pulp mill of 20 tons daily capacity indefinitely."

However, at that time no definite information as to the area covered with bamboo was available. These data have now been supplied through a survey made in October, 1911, by Mr. Rafael Medina, temporary assistant forester of the Bureau of Forestry, under the direction of Major George P. Ahern, director of the Bureau of Forestry, and the most important parts of the report are given in the following extract.

As a result of this work, two contiguous areas of *caña bojo*[2] were located; the first (block A) is embraced between kilometers 51 and 61 of the Patrol Trail, the Tama River, Botadero Creek (a tributary of the Tama River), the *sitio*[3] Salapungan, the Orani River, and the *sitio* Album; embracing an area of approximately 1,200 hectares of which it can be said with certainty that 800 hectares contain dense *bojo*. The second area (block B) is comprised between kilometers 62 and 66 of the Patrol Trail, the Bacon River to the *sitio* Baldugan, and the *sitio* Alupag, taking in an area of approximately 650 hectares, of which rather more than 40 per cent is covered with *bojo*.

In addition, smaller areas of *caña bojo* are found along the Rivers Bamban, Binasao, Pinulot, and Bacon, which form the basin of the River Colo, and also in the basin of the River Malabo or Balsic.

This block is less heavily covered with *bojo*, containing a greater portion of timber trees. Its development can best be accomplished by means of a donkey engine and cable, avoiding

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[1] *This Journal, Sec. A* (1910), 5, 242. The value of bamboo pulp is discussed in an editorial in *Trop. Life* (1911), 7, 176.

[2] *Bojo*, a bamboo of the genus *Schizostachyum*.

[3] *Sitio*, a place.

the difficulty of the Tama River by a short Lidgerwood serial cable to the branch of the tramway, since the Bacon River can only be used as a waterway from kilometer 67 and the Tama River from 2 kilometers west of the *barrio*[4] Culis.

For the development of block A, no waterway is available, so that it will be necessary to construct a tramway to carry the bamboo to the mill site.

The points which unite the best conditions for establishing the factory are the *barrio* Balut situated 3 kilometers north of Orani, and a point on the Orani River about 1 kilometer southwest of its mouth. Both have river or harbor connection with Manila Bay. The water of the former is salty, a disadvantage which can be overcome by using condensers. The bamboo can be assembled at both points from the basin of the Colo River and the Malabo or Balsic River. From either of the two points, a tramway can be established to kilometer 58 or 60 of the Patrol Trail (10 kilometers long) and from that point it can be made to branch off to the areas of *bojo*.

An area for reproducing *caña bojo* can be established by joining the two areas referred to above with the public lands situated north and east of them from kilometer 68, 3.5 kilometers in an easterly direction to the intersection of the two roads indicated on the map by the number 1; thence 5.5 kilometers in a southeasterly direction to kilometer 5 of the Patrol Trail from Mabaling to Orani; thence 1.5 kilometers in a southwesterly direction to the Orani River and following up the course of the river about 2 kilometers to the boundary of block A.

In all of the traversings made in this area, small areas of *bojo* have been found, especially in the ravines formed by the streams, and there are signs that areas which are now covered with *cogon*[5] and brush were formerly covered with *bojo*.

According to the information obtained from Negritos and other homesteaders and *caiñgineros*[6] of the region, *caña bojo* can be reproduced in the same way as spiny bamboo;[7] that is, by cutting from the young cane tubes which comprise two nodes, making a cross-cut in the tube and covering it with earth, being careful not to cover the cross-cut in order that water and dew may get in. The *bojo* produces seeds which can be collected in the dry season. The best time for planting or sowing this

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[4] *Barrio*, one of the districts into which a town is divided.

[5] *Cogon*, a large grass, *Imperata cylindrica* Beauv.

[6] *Caiñginero*, one who makes a clearing in the forest for planting.

[7] Spiny bamboo, *Bambusa blumeana* Schultes.

bamboo is in the month of May or June at the beginning of the rainy season, since it requires a great deal of moisture for its development. One person can plant in a day about 400 prepared tubes, or he can prepare from 1,000 to 1,200, if the growing areas are not very far apart.

There is attached a topographical map of the *bojo* area, showing its density and the easiest routes for its transportation.

R. C. McGREGOR.

ILLUSTRATION.

MAP 1.

Map showing areas of bamboo (*caña bojo*) in Bataan Province, Luzon. (Redrawn in the division of mines, Bureau of Science, from data furnished by the Bureau of Forestry.)

125
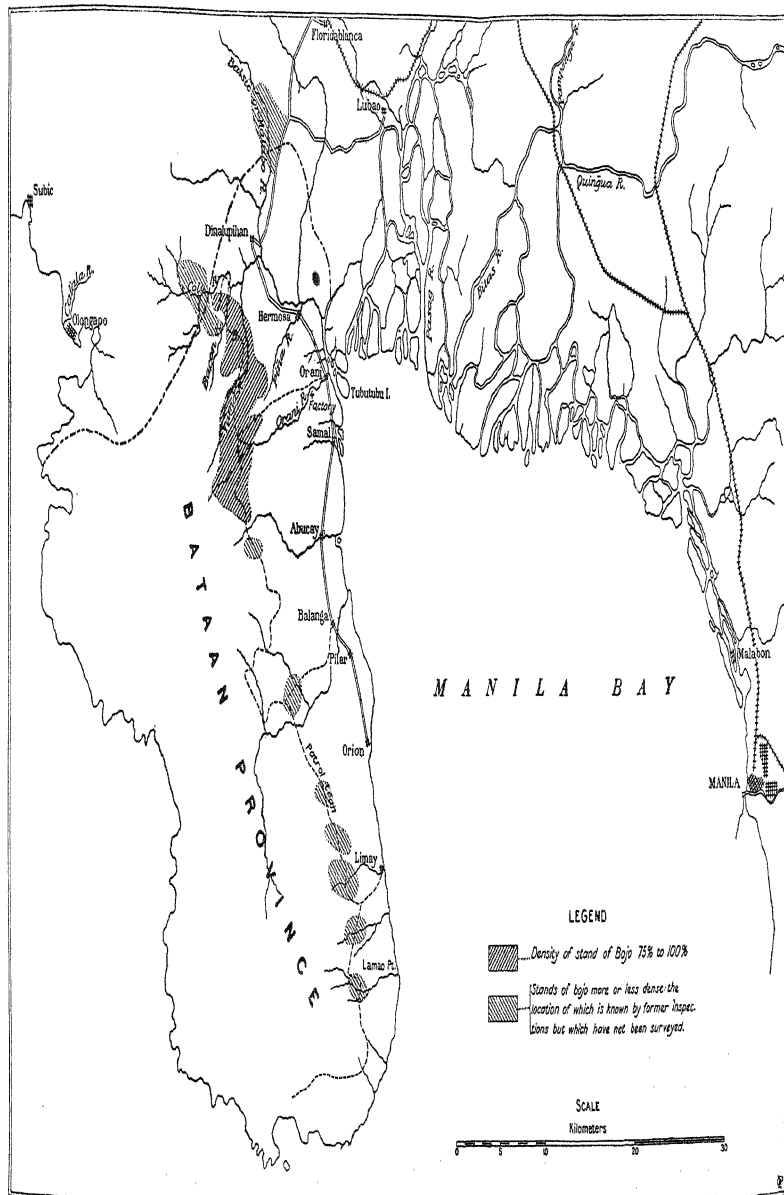
MAP 1.—Areas of bamboo (caña bojo) in Bataan Province, Luzon.

REVIEWS.

This book consists of an introduction, Part I, meats and meat products; Part II, poultry and eggs and game birds; Part III, fish foods; Part IV, milk and milk products and oleomargarine; Part V, cereal foods; Part VI, vegetables, condiments, fruits; Part VII, vegetable oils and fats and nuts; Part VIII, fungi as foods; Part IX, sugar, sirup, confectionery, and honey; Part X, infants' and invalids' foods; Part XI, simple methods for detecting food adulterations; appendix, food standards, and an index.

This work is more complete than the first edition and the treatment of the subjects is in the same broad and liberal style. The information is given in a form which is readable and readily understood by the layman and housekeeper; and, while the food chemist will refer often to the volume, it is not designed to be a working manual. Housekeepers and purchasers of foods, who familiarize themselves with its contents, will reduce the cost of living and improve the quality and palatability of their viands.

Dr. Wiley's book is the result of many years of investigation and strife for pure food in America.

H. D. G.

For several years teachers of college physics have felt the need of better and more modern texts suitable as the basis of class room work. That the need has been almost universally recognized is evident from the number of college texts that have appeared during the last year. New books by Crew of Northwestern, Carhart of Michigan, Magie of Princeton, Kimball of

Amherst, Hurst and Lattey of Oxford, England, Spinney of Iowa, added to those already in the field, make possible the selection of a text adapted to the particular conditions and aim of a given course.

An addition to the above list is the recent book by Professors Reed and Guthe, of the University of Michigan, which, without doubt, will be received with interest by many instructors of college physics. The threefold aim of the book, as expressed in the preface, namely "(a) to present the fundamental facts of physics in a clear, concise, and teachable form; (b) to relate the fundamental facts to the basic laws and to the theories of physics in such a way as to render plain the historical growth of the science; (c) to put the student in direct touch with first hand information concerning the epoch-making discoveries of the past upon which the growth of the science has been based, as well as to afford an intimation of the marvelous progress of the present" has for the most part been admirably attained. Unless one is a firm believer that the best order of presentation is that which follows closely the historical development there can scarcely be any objection to the order in which the subject matter is arranged, except possibly in the treatment of the subject of current electricity before that of electrostatics. In this case the historical arrangement would seem to be the logical one, a knowledge of electrostatics being of fundamental importance in the study of current electricity. Moreover, the study of the more interesting subject of current electricity is apt to detract from the interest which would otherwise be manifested in electrostatics.

The authors are certainly to be commended on their third purpose, the attainment of which is largely due to a wise selection of references to original papers, which will enable the ambitious student to develop a spirit of inquiry into the methods employed in research, at the same time giving good examples of the logical interpretation of experimental results.

The relative proportions of the book devoted to the different branches of physics does not vary greatly from the average of the more recent texts, with the exception that mechanics receives slightly less attention than the average, occupying about 13 per cent of the text, while the subject of radiation, with 7 per cent, receives somewhat more than the average amount of space. About 22 per cent of the book is devoted to molecular physics and heat, 8 per cent to sound and wave motion, 26 per cent to electricity and magnetism, 23 per cent to light, and 3 per cent to the electron theory. The 3 per cent devoted to the electron

theory, including radioactivity, seems scarcely adequate in view of the remarkable advances made in that field within the last few years and especially when one considers its important bearing on the theory of all electrical phenomena.

Lists of problems with answers are given at the end of most of the chapters. The problems are well chosen and sufficiently numerous to give the student the necessary practice in mathematical physics. Educational experience would seem to show that the pedagogical value of the problems would be greater without the appended answers. The mathematical formulæ and physical quantities and constants scattered throughout the book are well chosen and adequate to meet the demands of the ground covered.

There is a tendency throughout the book to describe phenomena without seriously attempting to give a clear or adequate exposition of the underlying theory, even in those cases where the theory is fundamental and easily comprehended by elementary students. The authors seem to have accepted Spencer's definition of Science as classified knowledge and consequently overestimated the value of mere subject matter. In many cases the exposition is decidedly less satisfactory than that to be found in the elementary texts in use to-day in secondary schools and any student who has had a thorough first course in physics can not help but feel disappointed in a college text which merely adds to the subject matter without any corresponding addition to the theory of phenomena previously studied.

The book is well indexed and, for a first edition, remarkably free from typographical errors. The illustrations, type, and general appearance of the book are good, and teachers searching for a satisfactory text in physics will review it with pleasure.

J. R. W.

A Text-book of Physics. By Louis Bevier Spinney. Cloth. Illustrated. Price $2.75 net. New York. The Macmillan Company. 1911.

Among the more recent texts of physics, the one by Professor Spinney of the University of Iowa deserves especial attention. Although designed primarily for use as a text in courses offered to engineering and technical students, its field of usefulness should not be limited to any particular class of students. The clear, concise, and logical method of presentation of the fundamental laws combined with well-chosen illustrations of their application to technical work should make the book exceedingly popular as the basis of class-room work in general college physics.

While the illustrations exemplifying the fundamental laws and principles are chosen largely from industrial applications, the principles are not hidden under numerous details, both the descriptions and the accompanying diagrams emphasizing simply and plainly the principles involved. The diagrams are not merely sketches of machines and industrial processes but rather working diagrams showing the manner in which the physical laws have been applied in concrete cases.

It is a pleasure to note that the author has not made the mistake, so common with writers of college texts, of attempting to describe every known physical phenomenon to the exclusion of a clear exposition of the more fundamental laws, but has wisely chosen the more important, attempting to give of each a clear, concise explanation. Fine distinctions and more or less tentative theories are wisely avoided, being left to more advanced treatises to which they rightly belong.

The book is divided into five distinct parts under the respective titles of Mechanics, Heat, Electricity and Magnetism, Sound, and Light. The subject of mechanics occupies about 26 per cent of the total space, heat about 14 per cent, electricity and magnetism 30 per cent, sound 10 per cent, and light 17 per cent.

The space devoted to mechanics is slightly greater than the average of the more recent texts, the topics of vector analysis, force and torque, accelerated motion, work, energy transformations, moment of inertia, and the kinetic energy of rotating masses being given special prominence.

The treatment of heat is very satisfactory, especially the chapters on the kinetic theory of gases, vaporization and solidification, and thermodynamics. The subject of radiation hardly receives the attention which its importance would justify.

The space devoted to electricity and magnetism is in harmony with the relative importance of the subject to technical students, a considerable portion of the space being devoted to descriptions of the underlying principles of modern electrical machines and industrial appliances. The illustrative diagrams of this part of the book are deserving of special notice, being well chosen and devoid of all unnecessary detail.

Preceding the discussion of sound and light is a concise presentation of the fundamental principles of wave motion. In the paragraph on the velocity of water waves the formula for the velocity is given without any attempt to derive or prove it. In my opinion an unproved formula is rarely, if ever, justified in an elementary text.

In the treatment of the subject of light, no effort is made to distinctly separate geometrical and physical optics. The topics of photometry and color receive more than the usual amount of attention, the treatment being exceptionally satisfactory. As elsewhere throughout the book, the diagrams are good.

Teachers who believe that the average student can be interested in physics most easily by relating closely the laws of physics to their industrial applications will be pleased to see a wide introduction of the book as the basis of class-room work.

J. R. W.

Theoretical and Physical Chemistry. By S. Lawrence Biglow, Ph. D. Cloth. Pp. XIII+544. Price $3. New York. The Century Company. 1912.

This work, the result of many years of study by one of the leading men in chemistry, comprises, as the author states in his preface, as much of the subject as can advantageously be presented in two or three lectures a week through one year. It is primarily a textbook for students who have a little knowledge of chemistry and the more advanced mathematics have been simplified or omitted as much as possible. In fact, with this book the author so presented the study that ordinary arithmetic and elementary algebra are all that are necessary, except in five or six demonstrations where calculus is used. Of course, this simplification makes it almost impossible to follow some of the later developments of physical chemistry, but when the purpose of this book is considered it can not be criticized.

The subject matter is divided into four sections. Quoting from the author's preface, these sections may be summed up as follows:

"The first section (three chapters) aims to show the value of philosophy in science. In the second section (seven chapters) the ever present question is: What are the ultimate constituents? In the third section (nine chapters) we are, primarily, studying the properties of substances as such, and in the last section (eleven chapters) our attention is centered upon the processes by which substances become what they are."

The relation of the science of chemistry with the mother science, philosophy, is carried out admirably throughout this work, and, although subjects are presented upon which volumes could be written, the selection of topics is in accord with the purpose of the book.

F. B. B.

Earth Features and their Meaning. An Introduction to Geology for the
   Student and the General Reader. By William Herbert Hobbs. Cloth.
   Pp. xxxix+506. Price $8 net. New York. The Macmillan Company.
   1912.

This work is illustrated in a manner very suitable to the
character of the production. There are 24 well chosen plates
and 493 text figures the majority of which are pen sketches.

The object of the book, as stated in the preface, is to furnish
a comprehensive discussion of the "dominant characteristics of
the different earth features and the geological processes which
have been betrayed in the shaping of them," presented in such a
manner as to appeal to the student and the general reader.
This object has been admirably attained. The theoretical dis-
cussion in relation to earth history, earthquakes, volcanoes,
weathering, erosion, and glaciation is excellent. The discussion
on each of these subjects is very extensive, presenting in the
majority of cases the latest accepted theories with the arguments
by which the various conclusions were reached. At the close of
each chapter are given numerous references which are in them-
selves a great additional value to the book. However, in the dis-
cussion of volcanoes are a few points which are open to criticism.
A careful examination into the reference given on Taal Volcano
will show that while quoting the Philippine Journal of
Science, section A, volume 6, number 2, as a reference the author
fails to use the information furnished, but nevertheless makes
statements either absolutely erroneous or grossly exaggerated.
The following errors on pages 120–121 are noted: Taal did not
erupt from two vents simultaneously, and text-figure 116 erro-
neously depicts such a condition. Taal is not 50 miles south of
Manila but 37. Taal, instead of lying dormant for 150 years, as
stated, has erupted twice during that time, in 1904 and in 1908.

The remaining statements, of loss of life on the island, loss
of life by poisonous gas, and by the great waves are much exag-
gerated. Only 106 bodies were found on Taal Island. No evi-
dence of death by poisonous gas was discovered. These deaths
were probably caused by suffocation and the breathing of steam.
The wave mentioned in no case traveled a half mile. In one
place it advanced about one-fourth of a mile and washed away
a few poorly-built nipa shacks. Furthermore no mention is made
of the most significant feature of the eruption as shown by Mr.
Pratt; that is, that no freshly-formed ash or recently-molten
rock was thrown out.

Another point for criticism is in relation to Mayon Volcano,
page 123. Mayon is discussed as a typical cinder cone. As

shown by recorded observation Mayon is a composite cone.[1] In fact, according to Abella,[2] it is more nearly a lava dome, and, since Abella probably had the best opportunities for observation, it might be stated that the weight of evidence points toward its being a lava dome.

These errors in regard to the only examples with which the author of this criticism is personally familiar would tend to discredit all of the examples cited in this voluminous publication. They show at least that the preparation had been done in a most careless manner, a condition especially to be deplored since the book is intended to be a textbook for students and especially adapted for university work.

Appendix B might be criticized as being too general. The definition of granite and syenite as being sometimes porphyritic differs from the classification of such well-known authorities as Kemp, Iddings, Cross, Pirsson, Washington, and Hatch who make a definite and distinct differentiation between granite and granite-porphyry.

F. T. E.

[1] *This Journal, Sec. A* (1911), 6, 464.   [2] *Ibid.,* p. 467.

PHYSICAL AND CHEMICAL PROPERTIES OF PORTLAND CEMENT. PARTS IV AND V.

By W. C. REIBLING AND F. D. REYES.

(From the Laboratory of General, Inorganic and Physical Chemistry, Bureau of Science, Manila, P. I.)

PART IV.—THE STRENGTH OF PORTLAND CEMENT.

INTRODUCTION.

The most important as well as the most elusive and subtle problem met with in the consideration of the hardening of Portland cement is in respect to the development and permanency of its strength.

Normal cement burned in the old dome and ring kilns seldom attained great early strength. The later, rapid development of the rotary-kiln process in the United States soon uniformly produced a Porland cement which hardened very rapidly. As such cement aided rapid construction work, consumers were eager to secure it. They even went so far as to offer a bonus for sound cement which would give exceedingly high 7-day tests.

However, it soon became known that this sound, high testing, rotary cement usually developed an abnormal decrease in strength which was not characteristic of the sound, slower hardening, set-kiln products.

At first this retrograde movement was thought to be character-istic of only the neat tensile strength determinations, but now it is

known usually to occur in the 1 : 3 sand briquettes as well. Many attribute this drop in tensile strength to brittleness, to unequal hardening, to a twisting action of the clips, or to an uneven application of the load, and maintain that it is not due to a disrupting action in the cement itself. Their final argument in this respect is that cement is seldom, if ever, used in tension and that the compressive strength does not experience this drop if sound cement is used. In fact, many investigations showed that in time the set-kiln cements often gave the best results. Such observations induced greater conservatism in the demands for strength in cement specifications; but, owing to the failure of Le Chatelier and others to ascertain the significance of the early gain in strength and the lack of knowledge concerning the chemistry of the hardening process itself, there have resulted divers conclusions, which more refined methods of manufacture and testing served to augment rather than to eliminate.

A consideration of the mechanical stresses involved in the resistance of concrete to compression indicates that the compressive strength of concrete should depend more or less upon the tensile strength of the cement used. The strength of mortar and concrete in compression is really their strength in shearing, and for a granular material the strength in shearing would be expected to vary with the strength in tension. The tensile strength of the cement is also related to a great extent to the factors which bind the aggregates together, and which tend to prevent disruption and wedging of the coarser copards when concrete is subjected to compression. In spite of this, it appears that no definite relationship has been established between the two. However, it finally has been shown that the compressive strength may not develop a uniform, nor a uniformly regulated, increase between different periods of time. In fact, the compressive strength of sound Portland cement mortar and concrete often shows a drop as decided as that of the tensile strength.[63]

The early failure universally to recognize the truth in this respect can be partly accounted for by the difference in the size of the specimens used for tension as compared with those used for compression. For an exact relationship, it is essential that the size of the specimens should always be the same. The outer and inner parts of mortar and concrete specimens do not harden at the same rate. Chemical analysis has repeatedly shown this

[63] *Bull. U. S. Geol. Surv.* (1908), **No. 331.**

to be true, but in many cases the difference is perceptible even to the eye. Most cement testers have noticed the inner core of almost dry mortar in freshly broken briquettes. The size of this core varies with the age, permeability, and nature of the cement, and the penetrating power of the reacting substances. For any given penetrating effect the value of the ratio of the zone influenced to the remaining interior decreases as the volume increases. Consequently, large specimens are less apt to show the peculiarities of cement than small ones. Also, as a retrograde movement in the cement near the surface may be counteracted by a development of strength in the inner material, and *vice versa,* we find that 2.54-centimeter specimens are more apt to give compressive tests showing the up and down values characteristic of 2.54-centimeter tensile briquettes than the 5.08-centimeter cubes so universally used.

The size of the specimens also influences the value of the ratio between the tensile and compressive strengths. For instance, when 5.08-centimeter cubes were used, all writers agreed that the value of this ratio was between 8 and 12 for 1 : 3 mortars. However, W. Pruves Taylor[64] recently conducted a long series of tests in which he obtained compressive strengths of small cylinders 2.54 centimeters high and having a diameter giving an area of 6.45 square centimeters. These tests gave ratios the values of which averaged but slightly over 4 for the ordinary 1 : 3 mortar with quartz sand. Taylor says that—

another frequently made statement that tests in compression show a uniform increase in strength between different periods is not borne out by these tests, the strength in compression showing the common up and down values of sufficient frequency and amount to preclude the possibility of being caused by error.

However, as Taylor further remarks, it still appears that—

the values do not go up and down together, showing that not even for a single test can the ratio be considered a constant quantity, and that tensile and compression strengths are really entirely distinct properties and are only interdependent to a slight degree.

Our experience in crushing the halves of the briquettes broken in tension has also demonstrated the up and down values of this test. Sometimes the changes in compression coincided with the changes in tension and very often the direct opposite was true; but here, too, we have unlike conditions, the area of the cross section of the broken halves being considerably larger than the

[64] *Amer. Soc. Testing Mat.* (1906), 6, 389.

area fractured in tension. Under similar conditions, Portland cements which are undeniably weak in tension always attain a much lower strength in compression than those strong in tension. It would seem that discrepancies between the two values would not occur unless caused by contending influences which affected the conditions imposed by the tests in an unlike manner. It may be observed that such forces are at work when the values of the tension and compression tests fail to rise or fall coincidently.

There are many who advocate the substitution of compressive tests for our standard requirements in tensile strength, but nothing would be gained by such a change. Tension tests are more useful in revealing the true character of metals than any other kind of mechanical test, and they should be equally valuable to cement users. However, no test becomes of value until its significance is thoroughly understood, and failures properly to interpret the results obtained from tension tests of cement have had more to do with the general lack of knowledge on the subject under discussion than errors and imperfections in the mechanics of the test itself.

THE TYPICAL CURVE OF TENSILE STRENGTH.

Consider, for instance, the typical curve of tensile strength of Portland cement which, as described by W. P. Taylor,[65] rises sharply up to about twenty-eight days, then falls slightly until from two to six months, then increases up to one or two years and then falls off again as brittleness develops. Taylor believes that the first drop in strength is—

probably due to the different rates of hardening of the different constituents of the cement. The sulphates and aluminates harden very rapidly for a short period, and then soon fall to a very low value. The silicates, on the contrary, harden much more slowly, but their action progresses regularly with age.

This idea he illustrates in a general manner by a diagram which is reproduced in fig. 23.

Taylor failed to prove that the sulphates and aluminates in indurated Portland cement act as stated. The indurated aluminates prepared by Schott (Table XXXVIII) after being submerged in water for three months retained great strength. Our attempts to associate quantitatively this drop in strength with either the alumina, iron oxide and alumina, or sulphate in Portland cement, failed. We also found that it was possible to

[65] *Am. Soc. Testing Mat.* (1903), 3, 413.
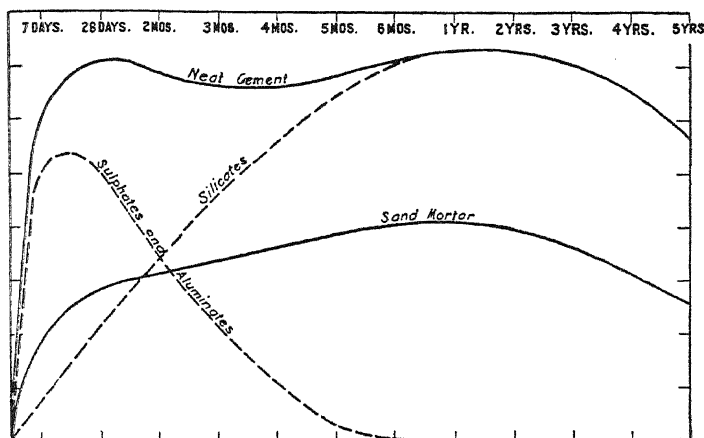
FIG. 23.—Typical curve of the tensile strength of Portland cement.

eliminate this characteristic depression almost at will. Therefore, it was necessary to search in other directions for the cause of this phenomenon.

THE INFLUENCE OF ULTIMATE CHEMICAL COMPOSITION AND EARLY GAIN ON STRENGTH.

W. A. Aiken [66] produced results and deductions from a large number of tests, the figures of which for five years—

corroborated his original assumption that an early stage, low-pulling cement which undoubtedly will show best results in the long run, can be made in the rotary kilns notwithstanding the general tendency of such commercial products to show abnormally high early results with a consequent retrograde movement later on.

He also conducted a long series of careful analyses and physical tests on the Lehigh Valley cements from which he fixed a theoretical analysis of material giving the highest ultimate results. However, he did not prove why this should be so, and his results have not been verified in tests on other than the few fresh commercial products with which he worked.

It was thought that an investigation on the variety of commercial Portland cements at our disposal would supply the data which were lacking. It soon became evident that Aiken's conclusions could have no general application. Sooner or later the

[66] *Cement Age* (1903), 1, 75.

cements recorded in Table A, Appendix 1,[67] developed the up and down values in the tests for strength. Sometimes a drop was met with soon after the first twenty-four hours, sometimes not until after six months, and the retrogression was apparently independent of the ultimate chemical composition, and bore no quantitative relation to the early strength developments.

It also became evident that the development and the maintenance of the early strength necessarily did not depend upon a narrow limitation of the percentage of lime, the value of the silica alumina ratio, the hydraulic index, or any other available chemical information. In most instances it was found possible to change the influence of all of these factors by altering the degree of burning, the fineness of either the raw material or the cement, and by seasoning the cement or the clinker to a different degree. This was true both for well-burned and under-burned cements, but more pronounced in the latter.

Our work showed that, as in the setting phenomena, changes in the condition of the free lime influenced the results of determinations of strength. As anticipated by E. B. McCready[68]—

no cements are perfect as regards to the chemical composition and the rate at which the disruptive strain due to free lime increases in different samples under various conditions of burning, grinding and testing, is the kernel of the nut which we ought to crack before placing too much reliance on rules deduced simply from analyses or percentages of gain.

The microscopical physical and chemical observations published in Parts I, II,[69] and III [70] of this paper have thoroughly demonstrated the existance of free lime in Portland cement, and a consideration of the chemical and physical properties of lime is in itself sufficient proof that it necessarily must exert an important influence on the development and maintenance of the strength. Our previous work has demonstrated that different methods of burning, grinding, and seasoning produce alterations in the physical and chemical properties of this free lime.

THE EFFECTS OF ANHYDROUS FREE LIME.

Although the presence of uncombined magnesia in a thoroughly burned cement may produce a gradual expansion which will cause mortars and concrete to disintegrate after several years, the usual cause of unsoundness is latent expansion due

[67] *This Journal, Sec. A* (1910), **5**, 415.
[68] *Cement Age* (1905), **5**, 339.
[69] *This Journal, Sec. A* (1910), **6**, 367 to 418.
[70] *Ibid.* (1911), **3**, 207 to 252.

to the slaking of free lime, and much depends upon the condition of the free lime and upon the influences to which the cement is subjected before and after it has set as to whether its presence will cause disintegration or weakness.

It is the lime which fails to slake before the cement has set that tends to cause disintegration. Lime which has been burned at a low heat and then finely ground hydrates within a very few minutes after being brought in contact with water. On the other hand, lime which has been burned at the white heat of the Portland cement kiln hydrates much more slowly and expands much more than lime burned at a low red heat. Consequently, a large quantity of anhydrous free lime may not cause natural cements to warp or crack, whereas as little as 1 or 2 per cent in hard-burned Portland cement is apt to cause disintegration.

The evil effect which free lime is capable of producing also depends more or less for its development upon the manner in which the cement is used and exposed. In general it may be stated that the expansion due to free lime in indurated Portland cement occurs within a few hours when it is submerged in boiling water or steam. Under water, at ordinary temperatures, it occurs mostly during the first seven days and is apparently complete by the end of two months. It is still slower when exposed to the air.

These observations are based upon the action of small experimental specimens. The ability of water or air to attack free lime in cement depends upon the density and volume of the mortar or concrete. Neat cement is almost impervious when it has hardened without cracking, and so also is a 1:1 or even a 1:2 well-mixed and indurated quartz-sand mortar. Therefore, the expansion due to free lime will not develop equally on specimens of different shape, volume, or density. It would manifest itself less in lean than in rich mortars, and the action of the lime will be rendered less harmful in natural sands containing pozzuolana than in the coarse, standard, quartz, testing sand.

It is the object of the boiling or steam tests to determine the presence of slow-slaking lime. If a Portland cement passes the hot test, it may be used immediately with reasonable certainty of its ultimate soundness. McCready [71] has called attention to the fact that the destructive force due to free lime and manifested in the boiling test "may not develop its full

[71] *Loc. cit.*

value in a month or a year. Cements unsound in hot water
and sound in cold disintegrated if boiled after six months in
cold water." The failure of the lime to slake in six months
can be attributed to the impermeability of the hardened neat
cement to cold water. The instances given in Table XXXVII
show that a cement which contains slow-slaking lime not only
may remain sound in boiling water, but also that ordinary
boiling with water may fail to slake all of the free lime in a
hardened cement.

TABLE XXXVII.—*The effect of the condition of the free lime upon the
soundness.*

Source of the cement.	Fineness.		Microscopic free lime test.	Soundness.	
	200 mesh.	100 mesh.		5-hour steam test.	28-day water test.
	P. ct.	*P. ct.*			
Ground, well-burned, nonseasoned clinker.	93.6	100	Some anhydrous sintered lime.	Not warped. Not cracked. Hard.	Sound.
Ground, under-burned, nonseasoned clinker.	76.1	94.0	Considerable sintered, nonsintered, and some slaked lime.	Completely disintegrated and badly swollen.	Completely disintegrated.
The same aërated 8 days.	7.61	94.0	No active free lime_.	Sound _.	Sound.
The same (aërated 8 days) and reground.	94.0	1.00	Sintered, nonsintered, and slaked lime.	Slightly disintegrated and rather soft.	Do.
Commercial cement "N" as received.	76.4	95.6	Some sintered, nonsintered, and slaked lime.	Sound _.	Do.
Same reground ___.	99.0	100	Same, but greater in amount.	Disintegrated ___.	Do.

The failure of boiling water to attack the free lime in the
aërated cement until regrinding had been resorted to, can be
attributed to the impermeability of coatings of slag or calcium
carbonate surrounding microscopical particles of free lime.
(Table VI in Part I.) Therefore, we can extend McCready's
conclusions and state that even sound cements may contain free
lime the destructive force of which may not develop in a month
or a year.

Obviously the force which operates to cause cements and
mortars to disintegrate will not become apparent to the eye until
it has overcome the strength of cohesion developed by other con-
stituents in the cement, but it can not operate at all without
weakening the force which binds the particles together. Conse-

quently, if a hardened cement contains anhydrous free lime the strength which it otherwise is capable of developing and maintaining is certain, sooner or later, to be affected when this lime is permitted to slake.

THE EFFECTS OF SLAKED LIME.

The influence of slaked[72] lime on the strength of Portland cement is also affected by the nature of the cement and the manner in which it is used.

This is made apparent by a consideration of the properties of slaked lime which concern its efficiency as a mortar constituent. Water combines with lime to form calcium hydroxide, an absolutely dry powdery substance. When water is added to this powder, the bulk is much reduced and it may be worked into an extremely rich and unctuous paste. This paste when sealed in an air-tight receptacle undergoes no change and possesses no inherent power of solidification. When permitted to dry it shrinks and forms a porous mass of no great hardness. Because of the great shrinkage of lime paste which accompanies its drying, it can not be used neat, but must always be mixed with several times its volume of sand.

It is necessary to distinguish between this so-called "set," which is due to the mere drying out of the lime paste and a slight deposit of calcium hydroxide crystals, and the actual induration which is due to the gradual absorption of carbon dioxide. If the slaked lime is exposed to the air, these three processes may all go on more or less simultaneously. However, the presence of too little or too much water may wholly prevent the actual induration of slaked-lime mortars. According to Mr. Clifford Richardson,[73] if the mortar contains more than 5 per cent of water, the absorption of carbon dioxide does not go on. While the mortar contains as much as 0.7 per cent, the absorption continues. His tests also show that the mere drying out of the mortar is sufficient to enable it to resist the pressure of masonry, while further hardening furnishes the necessary bond.

The actual induration of lime mortars takes place very slowly and it is confined more or less to exposed surfaces and porous places where the air is able to penetrate. In certain thick walls and massive impermeable mortars, the slaked lime has failed thoroughly to harden after ages. Cox[74] attributes the extreme hardness of the mortar used in the old buildings in the Philippines to the porosity of the stone employed.

Pure slaked lime does not possess the ability to harden under water, but hydraulic properties may be imparted to it by the addition of pulverized materials, such as volcanic tufa, granulated blast-furnace slag, clay, brick dust, and in fact any substance which will furnish soluble or

[72] Slaked lime, which is amorphous, should not be confused with crystalline calcium hydroxide. It is known that some pure limes burned at very high temperatures can be hydrated but not slaked, showing hydraulic properties (see also Part III, page 234).

[73] Taylor and Thompson, Concrete, Plain and Reinforced. New York (1907), 53.

[74] *This Journal, Sec. A* (1908), 3, 410, 411.

hydrous silicic acid. The process of hardening in this case is also slow and tedious and more or less confined to the superficial surfaces of the particles, and for permanency in air requires constant or continuous moisture.

Under certain conditions the presence of slaked lime in cement may influence the strength mechanically, inasmuch as it affects its troweling properties and in certain conditions increases the impermeability of the mortar. However, to increase the impermeability, it can only be used to advantage with mortars leaner than 1 : 2, as it appears impossible to replace with this material the water which separates the grains of cement, or cement and sand, in neat pastes and 1 : 1 or 1 : 2 mortars, respectively.

THE EFFECTS OF COMBINED CALCIUM OXIDE.

The exact nature of the compounds formed and the chemical action involved in the hardening process of cement is more or less imperfectly understood, but recent years have contributed much to our knowledge of the physical factors. The influence of lime, which has entered into combination with silica, alumina, and iron oxide, on the strength has been the subject of much investigation.[75]

Schott fused various mixtures of nonfused ingredients containing calcium oxide and silica, alumina, and iron oxide in sufficiently large quantites to determine the soundness and tensile strength of the compounds produced. We have abstracted these tests in Table XXXVIII.

From these results it is apparent that pulverized fused compounds of lime and silica; lime and alumina (or iron oxide) ; and lime, silica, and alumina (or iron oxide) possess the property of hardening under water without an appreciable change in volume and without the necessity of preliminary curing unless free lime is present.

The extraordinary strength of the fused mixture obtained by adding from 5 to 8.5 per cent of alumina to the weight of the other ingredient is especially noteworthy. Within limits, the strength of the silicates increases as the lime increases, while with the aluminates the opposite is true. Portland cement is also usually manufactured from nonfused ingredients, but the raw materials are only heated to the point of incipient fusion

[75] Schott. The calcium silicates and calcium aluminates contained in Portland cement (translated by Dr. W. Michaelis, jr.), *Cement & Eng. News* (1910), **22**, Nos. 9 to 12; Keiseman, The hardening and constitution of Portland cement, *Cement & Eng. News* (1911), **23**, Nos. 1 to 4.

and the commercial product seldom gives a higher strength than 450 pounds per square inch in mortars composed of 1 cement to 3 standard sand. It is probable that perfectly fused Portland cements would be capable of attaining a higher strength than the sintered product of the present commercial practise.

TABLE XXXVIII.—*Properties of fused mixtures containing calcium oxide and various amounts of silica, alumina, and iron oxide.*

No.	Molecular proportions.	Melting point in degrees.	Raw materials.	Time of setting in minutes.	Soundness of neat and sand mortars in water.	Tensile strength of 1:3 sand mortars after 28 days in water.
1	1CaO, 1SiO2	1,300	CaSO4+SiO2	(a)	Disintegrated	0.0
2	2CaO, 1SiO2b	c1,900	CaO+SiO2	480—	Sound	150
3	2.5CaO, 1SiO2b	d1,900	----do	480+	----do	390
4	3CaO, 1SiO2b	d1,900	----do	480—	Disintegrated	0.0
5	1CaO, 1Al2O3	1,500	CaCO3+Al2O3	5+	Sound	795
6	2CaO, 1Al2O3	1,450	----do	(e)	----do	315
7	2.5CaO, Al2O3	1,450	----do	(e)	Sound if seasoned	105
8	3CaO, 1Al2O3	1,450	----do	(e)	Disintegrated	0.0
9	1CaO, 1Fe2O3	1,450	CaCO3Fe2O3	360+	Sound	120
10	2CaO, 1Fe2O3	1,500	----do	360+	----do	75
11	3CaO, 1Fe2O3	1,530	----do	10	Disintegrated	0.0
12	3CaO, 1SiO2+4.2 per cent Al2O3.	1,600	Ca O + Si O2— Al2O3.	120+	Disintegrated but sound after seasoning.	f585
13	3CaO, 1SiO2+5.0 per cent Al2O3.	1,600—	----do	×	Sound	535
14	3CaO, 1SiO2+7.1 per cent Al2O3.	1,600—	----do	×	----do	525
15	3CaO, 1SiO2+8.5 per cent Al2O3.	1,500	----do	×	----do	615
16	2.5CaO, 1S iO + 25C aO, 1Al2O3.	×	4 parts of fused 2.5 C a O, 1 SiO+1part of fused2.5CaO, 1Al2O3.	420	----do	420
17	----do	×	CaO, SiO2, and Al2O3.	420	----do	610

a Failed to set.   c About.   e Almost instantaneous.
b Stable modifications.   d Above.   f After seasoning.

The extraordinary strength of the mono-calcium aluminate is also especially noteworthy; and, taken as a whole, the experiments of Schott must be considered as definite proof of the incompetency of the ultimate chemical analyses to reveal the true nature of commercial Portland cements.

Schott took no measurements of the constancy of the volume of these indurated sound calcium compounds. However, the

work of E. D. Campbell [76] and others shows that the nearer we approach a thoroughly combined and fused clinker, the less the expansion of the resulting cement.

Keiseman's work shows the manner in which these compounds set and harden without an appreciable change in volume.

The fact that the hardening process of hydraulic, fused, calcium compounds is not limited to exposed surfaces, but takes place throughout the mass, is one of the main reasons that good Portland cements give the most constant and reliable development of strength in actual construction work.

THE EFFECTS OF FREE AND COMBINED LIME IN HYDRAULIC CEMENTS.

From an engineering standpoint, hydraulic cements may be classified in the following order of general usefulness and merit:

1. Portland cements.
2. Natural or Roman cements.
3. Pozzuolane cements made from blast furnace slag and slaked lime.
4. Hydraulic limes.
5. Pozzuolane cements made from natural volcanic matter and slaked lime.

The physical and chemical properties and the manufacturing requirements of the most efficient of these five classes of cements offer a remarkable demonstration of the properties of lime which have been discussed in the preceding pages. Typical cements of these five classes are known, the ultimate chemical analyses of which vary so slightly that they are within the limits of different Portland cements of standard quality. However, from the natural pozzuolane cements with their low tensile strength, low specific gravity, and slow, unreliable hardening properties, there is a rise in efficiency and usefulness through hydraulic lime and slag and natural cements to the great, reliable development of strength and the high specific gravity of good Portland cement. The great difference in these five classes of hydraulic cements is due almost entirely to the condition of the calcium oxide characteristic of each.

Natural pozzuolane cement.—Starting with the poorest, we have a raw mixture of hydrated lime and anhydrous silicious material. The latter reacts with the lime, and to this reaction hydraulicity is due. The wonderful durability of the pozzuolane cement used by the Romans is due largely to ideal climatic conditions and the porous, open-grained structure of the volcanic tufa used, as well as to the quantity of available silicic acid. These conditions are impossible or difficult to obtain elsewhere, and even were it not so, the extremely slow hardening process involved is so poorly adapted to meet the demands of modern construction work that the present

[76] *Amer. Chem. Soc.* (1904), **26**, 1273.

commercial importance of this class of cement consists principally in the fact that the addition of small quantities to Portland cement increases the resistance of the latter to the deteriorating action of sea and other impure waters.

Hydraulic lime.—Hydraulic limes and natural cements depend largely upon the same reaction for their hydraulic properties as pozzuolane cement; but here the burning process to which the raw materials are subjected increases the activity of the anhydrous silicic acid which increases the rate of hardening.

Hydraulic limes are used quite commonly in England, Europe, and in certain parts of the Orient where underburned set-kiln Portland cements are slaked, dried, and screened, and sold as hydraulic lime.

Natural (or Roman) cement.—Natural cements are largely used in America because of their cheapness. They harden more rapidly in air or water than hydrated lime, but generally speaking, they lack uniformity in strength, setting properties, and constancy of volume to a much greater extent than Portland cements.

Here in the Philippines much consideration has been given to the question of the possibility and the commercial feasibility of the local manufacture of cement.[77] The present and near future resources and the commercial and economic conditions of these Islands might favor the manufacture of what may be called an artificial Roman cement. Albert Victor Bleininger [78] makes the following summary in regard to the burning of natural or Roman cements:

"1. For Roman cements, high in lime, approaching the tri-calcium silicate and low in magnesia, the best burning temperature is 1000°. Such stone can be made into Portland cement by vitrification. This cannot be done successfully, however, with a Roman cement equipment, but requires more elaborate and expensive machinery and kilns.

"2. Roman cements, lower in lime than (1), and free from magnesia, can only be burnt at 1000°.

"3. Roman cements, high in magnesia, should only be burnt at 950°, as the great strength produced by making a magnesia Portland cement is counterbalanced by the danger of inconstancy in the volume due to the two rates of hydration of lime and magnesia, the latter hydrating only after the first has assumed a stony hardness, thus breaking the structure of the cement. In very sandy mortars and some kinds of work they might be used, but at this stage of our knowledge concerning cements they cannot be considered a safe proposition.

"4. Cements, dolomitic, less basic than the subsilicates, to be burnt only at about 950°."

Underburning tends to decrease the strength of these cements for the reason that more or less calcium or magnesium carbonate remains undecomposed and consequently inert.

[77] Cox, Alvin J., *This Journal, Sec. A* (1908), **3**, 391 to 407; (1909), **4**, 211 to 231; *Min. Resources P. I., Bur. Sci., Div. Min.* (1909); Pratt, W. E., *ibid.* (1912).

[78] *Bull. Geol. Survey Ohio* (1904), IV, 186.

The evil effects of overburning which long has been an established fact are very apparent from the curves of strength shown in fig. 24.

Gilmore [79] obtained these results by burning Ulster County, New York, cement in four stages represented by 1, 2, 3, and 4, respectively, where 1 stands for underburning, 2 for proper burning, 3 for overburning without vitrification, and 4 for vitrification. Gaetschenberger [80] obtained similar results with dolomitic marl from near Heidelberg.

The exact cause of the evil effect of overburning is but imperfectly understood. Bleininger suggests that the hydraulicity of natural cements is pozzuolane in character and that up to a certain temperature these calcarious mixtures are but pozzuolane-like, simple silicates, which on further application of heat become chemically more complex and non-, or but slightly, hydraulic. Bleininger failed to consider the alterations in the properties of the free lime at the various temperatures.

An overburned natural cement is essentially an underburned Portland
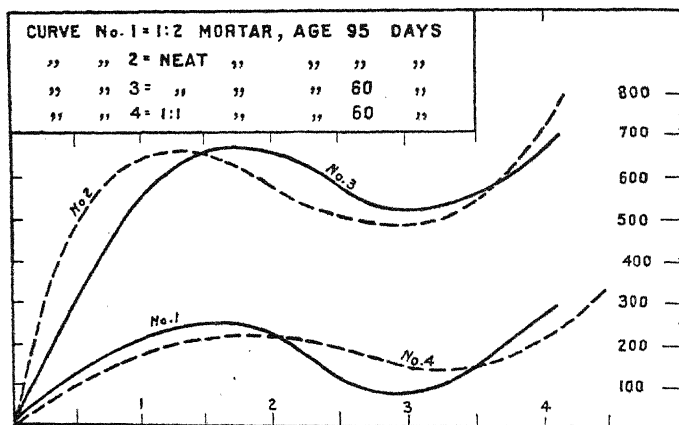
FIG. 24.—A diagram showing the evil effects of over-burning a Roman cement.

cement. In both instances the heat has been high enough to destroy the quick-slaking properties of the free lime, but not high enough to enable this calcium oxide to enter into combination. The manufacturers of natural cement well realize the evil effects of either under- or overburning their raw material. However, owing to the present universal practise of burning cement rock in set kilns and the variable chemical composition of the raw material, at times both under- and overburning are unavoidable, which explains the failure of these manufacturers to produce a uniform product.

To produce a more desirable cement of this class in the Philippines, we advocate the method of producing an *artificial* Roman cement by blending clay and limestone in the proper proportion and then burning the mixture at a low temperature in a rotary kiln. By this method the chemical

[79] Limes, Hydraulic Cements and Mortars (1870), 158.
[80] Quoted by Bleininger, *loc. cit.*

composition and the degree of burning could be uniformly regulated. It might not be a feasible method in countries where the cost of the production of Portland cement is low, but the high cost of imported coal and Portland cement in the Philippines would overcome this objection, and especially since local coals could be utilized for burning the natural cement.

Slag cement.—The manufacture of slag cement has not yet developed its maximum efficiency, although it will undoubtedly be perfected. They show their best strength when submerged constantly in water. The presence of calcium sulphide decreases their efficiency in works exposed to air and tends to cause a white efflorescence. The calcium hydrate which they contain also makes them liable to shrink and crack during the setting stage.

It has been thought that the sudden cooling brought about by quenching the molten slag converted it into true pozzuolane and that slag cements depend on the same reaction as pozzuolane for their hydraulic properties. This belief has little scientific foundation. If, as is generally assumed, slow cooling tends to break down or dissociate complex mineral compounds into simpler ones, it is evident that the quenching of molten slag would tend to prevent rather than to aid the formation of pozzuolane material. On the other hand, there appears to be every reason to believe that the severely criticised work of Zulkowski[81] leads to the correct conclusion that the hardening properties of basic slag and Portland cement are analogous; that is, due to the colloidal properties of the calcium silicates and aluminates. The liquid condition of the slag and its low lime and high silica and alumina contents make rapid cooling essential for the preservation of high-limed silicates and low-limed aluminates. Take, for example, a Chicago slag, the analysis[82] of which is given in Table XXXIX together with the composition of the silicates and aluminates formed at a high and at a low fusion temperature.

TABLE XXXIX.—*An interpretation of a Chicago slag.*

Available constituents.	Fused at a low temperature.	Fused at a high temperature.
Per cent. SiO_2 —32.20 Al_2O_3—15.50 CaO —48.14	The calcium oxide is sufficient to combine with all of the silica as $1CaO$, $1SiO_2$, and all of the alumina as $2CaO$, Al_2O_3. Also 1.1 CaO remains for the formation of higher limed aluminates. CALCULATION: 32.20 SiO_2 as $1CaO$, $1SiO_2$ requires 30.0 CaO. 15.5 Al_2O_3 as $2CaO$, $1Al_2O_3$ requires 17.0 CaO. CaO accounted for = 47.0 CaO available = 48.1 CaO by difference = 1.1	The calcium oxide available is not sufficient to convert more than about one-third of the silica into $2CaO$, $1SiO_2$. CALCULATION: 32.2 SiO_2 as $1CaO$, .$1SiO_2$ requires 30.0 CaO. 15.5 Al_2O_3 as $1CaO$, $1Al_2O_3$ requires 8.5 CaO. CaO accounted for = 38.5 CaO available = 48.1 CaO by difference = 9.6 9.6 CaO is capable of converting 10.3 SiO_2 from $1CaO$, $1SiO_2$ to $2CaO$, $1SiO_2$.

[81] *Chem. Ind.*, Berlin (1889), 12, 69.

[82] Eckel, E. C., *Mineral Resources of the U. S.* (1901).

These figures show that unless the slag is cooled very suddenly from a high fusion temperature it will contain very little strong cementive material and also that there is too little lime present to produce great strength under any conditions. Although this analysis is more or less theoretical it corroborates general practical experience that the more basic the slag, the better suited it is for cement making.

Portland cement.—Generally speaking, rotary-kiln Portland cement, and more so fused Portland cement, surpasses similar set-kiln products in strength and uniformity. Schott [83] showed that the crystalline structure of Portland cement clinker changed with the burning temperature independent of the percentage of lime which was the same in every instance, that Portland cement obtains its full development only at very high temperatures, and that at low temperatures, certain intermediary compounds are formed, namely, belite, celite, and felite, which do not harden to the same degree and which with increasing heat unite and form double compounds and ultimately represent a uniform mass (alite).

Owing to the unequal degree of burning to which the raw materials in different parts of a set kiln are subjected, and to fuel contamination, the aggregate produced by this process usually consists of a mixture of all five classes of hydraulic cements in which the well-sintered Portland cement clinker, typical of good rotary practise, predominates. For example, the weathered set-kiln products, the chemical and physical properties of which were described in Tables XVIII and XIX of Part II [84] of this paper, contained at least 15 per cent of underburned cement as well as some vitrified clinker. In Table XL we show the class and the source of its hydraulic constituents. We attribute the characteristic lower early strength of set-kiln products almost entirely to the presence of underburned material. This is at variance with the usual belief that the rapidity of the rotary process—more particularly the cooling down of the clinker—is the apparent cause of the greater activity of rotary cement. However, it already has been shown that there is no radical difference between the hardening properties of the pure well-burned product of these two kilns. Foreign matter from the fuel in the cement made by the older process often

[83] *Cement & Eng. News* (1910), 22, 377.
[84] *This Journal, Sec. A* (1910), 5, 410.

obscures this, as is shown by Table XLI, which gives the results obtained with seasoned, sound, rotary- and set-kiln products made at the same factory and from the same mixture of raw materials.

TABLE XL.—*A classification of various hydraulic cements found in the typical set-kiln products.*

No.	Source.	Identified constituents.	Classification.	Hardening process of the chief constituents.	Remarks.
1	Thoroughly fused clinker.	Various high temperature fusion products. No free lime.	Mostly fused Portland cement. Some slag from fuel contamination.	Colloidal____	The constant presence of water is essential to the greatest development of strength.
2	Hard-burned clinker (chief constituent).	Various high temperature fusion products. A little sintered free lime.	Typical well-burned rotary cement. Mostly fused Portland cement burned at a high temperature.	_____do _____	The constant presence of water is essential to the greatest development of strength. The evil effects of the small amount of slow-slaking free lime is usually not apparent to the eye.
3	Slightly underburned clinker.	Various low temperature fusion products and considerable sintered lime.	Typical over-burned Roman cement. Mostly fused Portland cement burned at a low temperature.	_____do _____	The poor strength derived from the low temperature fusion products is further reduced by the injurious effects of the comparatively large quantity of slow-slaking lime.
4	Underburned clinker.	Nonsintered lime, weak fusion products, and considerable pozzuolane material.	Typical artificial Roman cement and hydraulic lime.	Pozzuolane. Lime mortar.	A higher strength is attained in air than in water. The quick slaking properties make the free lime much less injurious than when sintered.
5	Nonsintered raw meal.	Nonsintered lime, dehydrated clay, and inert calcium carbonate.	Typical of artificial pozzuolane cement.	_____do _____	The lime mortar hardens only in the air. The pozzuolane cement requires constant or continuous moisture for permanency in air.

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TABLE XLI.—*The strength of rotary- and set-kiln products of brand O cement.*

No.	Material.	Fineness.		Specific gravity.	Tensile strength.									
					Neat.					1:3 Ottawa sand mortar.				
		200-mesh.	100-mesh.		7 days.	28 days.	3 months.	8 months.	1 year.	7 days.	28 days.	3 months.	8 months.	1 year.
1	Rotary cement ____	77.6	93.2	3.114	642	725	678	✕	752	296	338	330	✕	291
2	Set-kiln cement ____	79.2	95.4	3.093	503	614	637	✕	752	216	272	300	✕	289
3	Rotary cement ____	79.7	98.2	3.10	638	645	680	✕	708	240	298	313	✕	302
4	Sound clinker from set kiln ____	80.6	100.0	3.05	605	701	718	740	748	248	288	345	364	340
5	Disintegrated clinker from set kiln _____	77.6	100.0	2.794	290	391	495	582	600	88	144	224	245	275

Cements numbered 3, 4, and 5 contained 1.6, 1.5, and 1.5 per cent, respectively, of gypsum.

Cements 1 and 2 were typical examples of the better class, commercial, rotary- and set-kiln cements then produced by this factory. Cement 4 was obtained by separating the well-burned clinker from the other inferior, disintegrated products (5). Compared with a hard-burned rotary cement (3) of practically the same ultimate chemical composition and fineness, cement 4 shows the same characteristic features even to drop in strength of the one-year sand mortar values. The results obtained with cement 5 clearly demonstrate that the presence of underburned cement is the cause of the characteristic low early strength of the average set-kiln products.

The strength of our high-limed rotary products is not materially affected by quenching the clinker in water except in so far as this quenching affects the free lime, and rapid cooling is not essential to the preservation of the high-limed silicates and low-limed aluminates in Portland cement. There is little opportunity for molecular changes to occur after the clinker has begun to cool because the burning is accomplished very quickly and only reaches the incipient state, the percentage of calcium oxide is high, and the clinker cools fairly rapidly through the eutectic temperatures.

The strength of a cement increases with the burning temperature and, to a certain point, with the quantity of combined lime, and few Portland cements pass our standard specifications unless the clinker contains at least 60 per cent of calcium oxide and is sufficiently sintered to form the high-limed silicates and low-limed aluminates.

The soundness of the cements is a fundamental consideration, and the fact that our work showed that any tendency toward unsoundness developed more slowly in cold than in hot water, and still more slowly in air, verified the previous statements concerning the properties and influences of free lime.

Cements so bad as utterly to disintegrate when subjected to the boiling test have remained in the air for over a month without showing a measurable increase in volume. However, any tendency toward unsoundness is eventually very apt to become more pronounced in the air because the slaking lime increases its volume more in air than in water.

Our experiments show that the worst results are obtained if the hardened mortar is weathered outside and exposed to the sun and rain. Plate VII, fig. 1, is from a photograph of a cement which remained sound in water and air and almost passed the boiling test, but which disintegrated when exposed to the sun and rain. As several other cements remained sound after similar treatment, the destruction produced by weathering the mortar can not be attributed solely to the heat of the sun. Generally speaking, Portland cements shrink in the air and expand in water, and it is thought that the constantly humid and dry conditions of the weathered material tend to produce a maximum disrupting effect. Plate VII, fig. 2, shows the beneficial results obtained by regrinding the same cement.

The soundness is improved by the presence of sand and other suitable aggregates. The development of changes in volume is also largely dependent upon the permeability of the mortar; that is, the greater the porosity, the greater the possibility of rapid and uniformly distributed changes in volume.

Portland cements may be classified with respect to their soundness as follows:

(1) Cements which fail to pass all of the standard tests for soundness.

(2) Cements which fail to pass the accelerated tests, but which remain sound in normal air and water for twenty-eight days.

(3) Cements which pass all tests for soundness.

No consideration is given to Portland cements which warp, crack, or disintegrate so quickly in cold water or in air as to place them in class 1. However, it is usually possible greatly to improve the quality of such cements by properly seasoning them, the first effect of which tends to place them in class 2.

Some class 2 cements disintegrate sooner or later after the specified twenty-eight days have expired, while others remain sound and strong for an indefinite number of years; therefore, the significance of the hot test is very uncertain. This and

the fact that unsound cements may possibly, through subsequent exposure to the air before being used, or because of mixing with sand or other aggregate, produce durable masonry, has led to a somewhat general belief that failure to pass the tests for soundness, especially the hot test, is not a positive proof of inferiority.

On the other hand, further observations and experience have strengthened the early, published work of this laboratory, which led to the conclusion that perfect soundness was especially important to the efficiency of Portland cement used in the Tropics.

THE EFFECTS OF SEASONING.

Underburned Portland cement.—The data given in Table XLII show the general nature of the cement produced from decidedly underburned clinker.

If such material is used before it has seasoned it will act like sample 1, in which the disruptive force was sufficient to cause the complete disintegration of both neat and sand mortars soon after the cement had set. The first step toward a sound product is shown by sample 2. Here while the neat mortar also disintegrates, the sand mortar remains sound; although, as shown by the 3- and 7-day strength values, the expansion is sufficient to make its effect upon the strength apparent. The further seasoning of the cement soon eliminates this drop in strength. The neat mortar undergoes similar changes until eventually a product like sample 3 is obtained, which continues to harden and to show a slow but steady increase in strength for apparently an indefinite length of time.

The points which we wish to emphasize about soft-burned cements are that the clinker seasons very readily, that the hardening process is slow, and that ordinarily the expansion due to free lime occurs very soon after the set. The last is of special importance, since the expansion of the free lime in the indurated mortar develops so quickly that it is safe to assume the ultimate soundness if the neat mortar does not disintegrate after being submerged in normal water for the usual twenty-eight days.

The similarity between such underburned Portland and natural or Roman cements is very close. However, the presence of harder burned material in the latter makes its behavior less certain, for as is shown in Table XLIII the harder burned clinker possesses characteristics which are entirely different from those just described.

TABLE XLII.—*Characteristic hardening properties of soft-burned Portland cement.*

Sample number.	Cement.	Tensile strength in pounds per square inch.										Soundness of normal sand mortars.		
		Neat.					1:3 Ottawa sand.					5-hour steam test.	28 days in normal water.	28 days in air.
		3 days.	7 days.	28 days.	3 months.	1 year.	3 days.	7 days.	28 days.	3 months.	1 year.			
1	Nonseasoned, underburned cement	165	(a)				30	(a)	74	139	200	Disintegrated	Disintegrated	Disintegrated.
2	The same slightly seasoned	190	(a)				66	40	142	200	240	do	Sound	Sound.
3	The same well seasoned	×	200	280	340	400	×	86				Sound	do	Do.

a Disintegrated.

TABLE XLIII.—*Characteristic hardening properties of hard-burned, commercial Portland cements.*

Sample number.	Cement.	Tensile strength in pounds per square inch.											Soundness of normal neat mortars.		
		Neat.						1:3 Ottawa sand.					5-hour steam test.	28 days in normal water.	28 days in air.
		1 day.	7 days.	28 days.	3 months.	6 months.	1 year.	7 days.	28 days.	3 months.	6 months.	1 year.			
1	Nonseasoned, hard-burned cement	500	760	785	Disintegrated.			200	245	90	Disintegrated.		Disintegrated	Sound	Sound.
2	...do	470	720	785	745	800	707	296	360	360	375	320	do	do	Do.
3	...do	430	740	815	1,010	1,015	755	245	335	505	530	360	Sound	do	Do.
4	Seasoned, hard-burned cement	400	595	770	905	915	720	230	385	505	490	360	do	do	Do.

Hard-burned Portland cement.—The results obtained with these samples show that the hard-burned clinker may or may not produce a cement which requires no curing to enable it to pass the accelerated tests for soundness. Seasoned or nonseasoned cement, provided it passes the hot tests, may be used with reasonable certainty of its ultimate soundness. However, as is shown by sample 1, no reliance can be placed on the 28-day tests. Such material frequently attains a very high and increasing early strength, but afterward expands so much that eventually even lean sand mortars disintegrate. This fact is sufficient cause for the rejection of all Portland cements which fail to pass the hot test.

Sample 1 also shows the effect of high temperature on the slaking properties of free lime. The expansion due to this cause develops very slowly; so slowly, in fact, that it does not interfere appreciably with the early strength. The high temperature also induces the formation of the quick-hardening calcium silicates and aluminates, which accounts for the characteristic great early strength of the hard-burned cement.

We find that whereas the soft-burned cement continues to harden indefinitely, the strength of sintered products may be less at the end of years than it was at the age of twenty-eight or sometimes even seven days. The practical importance and the real significance of this great difference in the hardening properties of soft- and hard-burned cement is apparent from a comparison of the time strength tests of typical natural and Portland cements such as are given in Table XLIV.

The most efficient natural, or Roman, cements are composed mostly of soft-burned material while the hard-burned product very largely predominates in the Portland cements of good quality. Accordingly, as is shown in Table XLIV, it is characteristic of the natural cement sand mortar to show such a steady increase in strength that it eventually becomes stronger than similar mortars of Portland cement. This, and the relative cheapness of natural cement, have caused considerable discussion concerning the relative merits of the two products, and there are many who advocate the general use of natural cement in preference to Portland. However, the slowness with which natural cements harden hinders rapid construction work to such an extent that the use of Portland cement is usually advisable and very often actually necessary. Consequently, the greatest

economic efficiency in modern concrete construction depends upon perfections in the manufacture of Portland cement.

TABLE XLIV.—[a] *Time tests of the tensile strength of typical natural and Portland cements of good quality.*[b]

Mortar.	Tensile strength in pounds per square inch.											
	7 days.	28 days.	1 year.	2 years.	3 years.	4 years.	5 years.	6 years.	7 years.	8 years.	9 years.	10 years.
	"Giant" Portland cement (1894).											
Neat	547	699	666	645	673	678	668	642	631	659	676	689
1 : 2 sand	397	529	769	755	775	793	755	670	677	695	669	651
	"Union" natural cement (1894).											
Neat	159	245	460	453	443	458	465	540	493	515	427	
1 : 2 sand	89	190	526	574	599	635	677	775	728	744	737	837

[a] These figures are reproduced from a report by R. W. Lesley, *Amer. Soc. Test. Mat.* (1905), **5**, 324.

[b] Summary of Cement Tests on the New Croten Dam Division of the New York Aqueduct Commission representing a record of nearly half a million barrels of "Union" natural and "Giant" Portland cements.

Commercial Portland cement.—The character of the curves of tensile strength is influenced by the extent to which the cement has seasoned. The general effects of thorough aëration on sound commercial Portland cements are recorded in Table XLV (see Table A, Appendix I, Parts I and II, for the chemical analyses).

The cements described in Table XLV were all received in sound, paper-lined barrels and contained practically no cake. They had been sufficiently seasoned as they failed to show any tendency toward unsoundness when subjected to the accelerated tests. Therefore, the physical properties of these cements are characteristic of properly packed and stored, uninjured, sound products produced by the manufacturers.

The data recorded in Table XLV make it apparent that the tensile strength, and even the character of the curve of strength, of any given cement may be affected to a considerable extent by the method of molding employed or the quantity of water and the quality of sand used. In spite of these variable factors certain characteristics of Portland cement influence the strength to such an extent as to be readily apparent.

The specific gravity of even a hard-burned well-manufactured cement can be reduced to a low figure by thoroughly aërating the ground product, but this process reduces the early strength of a sound cement. The actual value of the change which excessive aëration produces is measured best by the results obtained from mortars of normal consistency, but as the aërated cement usually requires the most water it may be argued that the low strength is the natural result of a leaner mixture. However, the data recorded in Table XLVI show conclusively that the aërated cement is weaker than the original product.

TABLE XLVI.—*Tests of the tensile strength of cement M which show that the weakness produced by excessive aëration is inherent in the cement itself.*

Condition of the cement.	Method used for molding the briquettes.	Water used.	Tensile strength of 1:3 Tarlac sand mortars in pounds per square inch.			
			7 days.	28 days.	3 months	1 year.
		Per cent.				
As received	U. S. A. E	12.5	195	218	274	342
Aërated 3.5 months	do	13.5	96	155	215	347
Do	do	12.5	101	168	230	316
Do	do	10.0	128	171	201	282
Do	A. S. T. M	12.5	135	172	236	329
Do	do	10.0	131	175	238	266

The weakness of the aërated cement is the result of the conversion of slaked lime into calcium carbonate, and the tendency of this reaction to confine itself to the surfaces of the individual particles of cement shows that the strength is affected by retarding rather than by eliminating the activity of the hydraulic properties.

For instance, it is the finest particles of cement that are affected the most by aëration and in several instances we have succeeded in aërating very finely ground cement until it had apparently lost all power of hardening. However, it was found that if this material was left in the molds and later submerged in water it eventually hardened and in time gained great strength. Two instances of such an experience are given in Table XLVII.

TABLE XLIV.—General effects of seasoning on the strength of sound commercial Portland cements.

Sample number.	Brand.	Source.	Fineness. Time aerated. (Days.)	Fineness. Through a 200-mesh sieve. (Per cent.)	Fineness. Through a 100-mesh sieve. (Per cent.)	Specific gravity dried at 110°.	Amount of water required for normal consistency. (Per cent.)	Neat briquettes. Method of molding.	Amount of water used. (Per cent.)	Tensile strength per square inch. 7	28	90	360	1:3 crushed quartz sand. Method of molding.	Amount of water used. (Per cent.)	Tensile. 7	28	90	360	1:3 Ottawa sand. Method of molding.	Amount of water used. (Per cent.)	Tensile. 7	28	90	360	1:3 Tarbu sand. Method of molding.	Amount of water used. (Per cent.)	Tensile. 7	28	90	360
1	B	Average contents of one barrel.	100	70.0	90.0	2.88	23.5	A. S. T. M.	22.5	310	442	478		U. S. A. E. (1900).	12.5	55	141	228		A. S. T. M.	10.6	55	106	244	317	A. S. T. M.	10.0	101	207	330	
2	C	.do	0	76.6	88.1	2.79	27.0	.do	27.0	194	290	386		.do	12.5	77	124	190		.do	10.6	161	172	202		.do	10.8	138	202	260	
3	C	.do				2.89	34.5	.do	34.5	208	372	432	536	.do	12.5	125	210	280								.do	10.1	110	275	385	
4	C	.do	113			2.98	38.0	.do	38.0	313	208	242	289	.do	13.5	145		154								.do	11.8	147	193	245	
5	C	.do				2.99	27.0	.do	27.0	890	438	445	646	.do	12.5	138	213	292	297	.do	10.6	130	231	332		.do	12.5	183	227	279	
6	D	.do	60	80.2	94.8	2.95	30.5	.do	30.5	294	388	445	479	.do	12.5	116	166	196	247							.do	11	60	122	203	290
7	D	.do	90			2.91	30.5	.do	30.5	282	387	443	475													.do	11	88	121	287	284
8	D	.do			93.0	2.93	30.0	.do	30.0	672	737	686	686	.do	11.0	303	276	304	288	.do	11.0	89	181	274	286						
9	D	.do	40	77.4		3.11	24.0	.do	24.0	473	531	539	670	.do	12.5	137	220	251	274	.do	9.7	184	299	332							
10	G	.do	90		97.2	2.99	22.0	.do	22.0	555	580	576	676	.do	12.5	106	196	248	275							A. S. T. M.	11.0	151	180		
11	G	.do	0	88.4		2.08	34.0	.do	34.0	1.003 ± 515		589	603	.do		279															
										487	422	540	574			177	284	288	269												
12	H	.do	33			2.90	30.0	U. S. A. E.	30.0	314	384	434	500	A. S. T. M.	12.5	117	190	244													
13	H	.do				2.97	34.0	.do	34.0	460	477	496	513	.do	10.0	107	186	235													
14	H	.do	90			2.98	29.0	A. S. T. M.	29.0	270	373	400	400	.do	10.8	108	186	196	207												
15	H	.do	0	58.0	96.0	3.08	21.0	.do	21.0	545	538	248	611	U. S. A. E.	12.5	96	181	196								.do	9.5	183	344	321	423
16	T	.do	0			2.93	27.5	.do	27.5	298	464	490	535	.do	12.5	91	190	266								.do	10.6	101	255	308	388
17	T	.do		73.8	94.8	3.05	23.0	.do	23.0	506	546	545	550	.do	12.5	208	308	341								.do	9.8	207	266	334	383
18	M	.do	90			3.00	23.0	.do	23.0	440	522	572	522	.do																	
19	M	.do	90			2.91	36.0	.do	36.0	401	485	500	531	.do																	
20	M	.do	150			2.91	31.0	.do	31.0	365	459	470	517	.do	12.5	130	196	254	271	.do	11.1	125	209	315	277	.do	10.7	135	205	290	303

TABLE XLVII.—*Showing the effects of thorough, prolonged aëration on finely ground Portland cement.*

Brand.	Cement.	Specific gravity.	Tensile strength in pounds per square inch.							
			Neat mortar.				1:3 Ottawa sand mortar.			
			7 days.	28 days.	3 months.	1 year.	7 days.	28 days.	3 months.	1 year.
H	As received _____	2.97	460	477	498	503	205	301	350	290
H	Thoroughly aërated 4 months __	2.742	0	ᵃ20	297	320	0	143	284	289
N	As received, the residue remaining on a 200-mesh sieve being rejected _____	3.091	550	564	582	570	317	412	447	425
_____	Thoroughly aërated 100 days, the residue remaining on a 200-mesh sieve being rejected_	2.807	0	ᵃ20	365	ᵇ395	0	_____	280	ᵇ335

ᵃ Less than.
ᵇ One year and four months.

Owing to the protective coating of carbonate which surrounds the particles of aërated cement, the rate at which the inner active constituents become indurated depends upon the permeability and exposure of the mortar. A good example of this is the 28-day values of the aërated cement H. As recorded in Table XLVII, the sand mortar developed a strength of 143 pounds while the neat remained almost too weak to support the weight of the clips. As is shown in Tables XLVIII and XLIX, it was found that larger specimens, especially those which were not submerged in water, hardened so slowly that the time tests of aërated and nonaërated cement showed a greater difference than the briquettes.

TABLE XLVIII.—*One-year tensile and compressive strengths of aërated and nonaërated cement H in pounds per square inch.*

Cement H.	Specific gravity.	Average tensile strength of 1:3 sand mortar briquettes which were stored in water.	Average compressive strength of 3″ x 4″ cylinders of 1:3 sand mortar which were stored 7 days in moist air and then weathered outside.
As received _____	2.97	274 (efficiency = 100)_____	3,696 (efficiency = 100).
Aërated 90 days_____	2.83	222 (efficiency = 81)_____	2,280 (efficiency = 61.7).

TABLE XLIX.—*Compressive strength of weathered 6-inch concrete cubes made with aërated and nonaërated cement J.*

Cement J.	Specific gravity.	Proportions by volume.	Age in days.		Compressive strength.			
					Total in pounds.		Pounds per square inch.	
			In moist air.	Weathered outside.	60 days.	1 year 3 months.	60 days.	1 year 3 months.
As received_____	3.13	1:2:5	21	435	82,630	108,300	2,290	3,010
Aërated 90 days ___	3.00	1:2:5	21	435	45,115	84,450	1,250	2,350

It was to be expected that the original hardening properties of a normal Portland cement would be restored almost entirely if the impermeable coatings of carbonate surrounding the aërated particles were destroyed by regrinding. The instances given in Table L show the large extent to which this really occurs.

TABLE L.—*Tensile tests of hard-burned cements N and O showing the characteristic effect produced by regrinding after through aëration.*

Sample.	Brand.	Cement.	Fineness.		Specific gravity.	Tensile strength of 1:3 Ottawa sand mortars in pounds per square inch.[a]			
			200 mesh.	100 mesh.		7 days.	28 days.	3 months.	1 year.
			Per ct.	Per ct.					
1	N	As received _____	76.4	95.6	3.11	299 (2,400)	357 (3,160)	385 (3,510)	353 (2,990)
2	N	Sample No. 1 reground__	87.6	100.0	3.09	314 (2,780)	313 (3,400)	389 (3,350)	337 (3,450)
3	N	Sample No. 1 thoroughly aërated 20 days.	--------	--------	3.01	240 (1,670)	291 (2,350)	357 (3,290)	329 (3,600)
4	N	Sample No. 3 reground__	91.8	100.0	3.01	315 (2,430)	386 (3,080)	424 (3,860)	424 (4,240)
5	O	As received_____	77.4	97.1	3.100	272 (2,320)	322 (2,460)	333 (3,130)	302 (3,260)
6	O	Sample No. 5 thoroughly aërated 100 days.	77.6	98.0	2.955	194 (1,730)	284 (2,050)	361 (2,190)	338 (2,750)
7	O	Sample No. 6 reground__	89.4	98.8	2.950	326 (2,830)	385 (3,020)	409 (3,670)	419 (4,400)

[a] The figures inclosed in parentheses give the values obtained by compressing the broken briquettes.

A low specific gravity (dried at 110°) is always associated with a correspondingly low early tensile strength.[85] Of course,

[85] The strength developed by the aërated samples (numbers 4 and 7) after they had been reground offers an apparent contradiction to this statement. However, the assertion is made with reference to the commercial product, and as such we believe it true because no manufacturer goes to the great expense of thoroughly aërating his cement (a process

in this connection the fineness of the cement must be taken into consideration, but provided the cements are ground to ordinary fineness the general relationship seems to exist regardless of the cause of the low density.

The results given are characteristic of those obtained from our entire series of experiments. Aëration seemed to effect the early compressive strength of the broken briquettes and the tensile strength in a similar manner. The results obtained by crushing larger specimens which had been stored in the same manner as the briquettes (Table L) are given in Table LI.

TABLE LI.—*Compressive strength of 3″ × 4″ cylinders of 1:3 Pasig sand mortars showing the characteristic results obtained with aërated and nonaërated, soft and hard-burned cement.*

Brand.	Cement.	Specific gravity.	Constituents of 1:3 mortars.			Compressive strength in pounds per square inch.	
			Pasig sand.	Cement.	Water.	3 months.	1 year.
			Grams.	*Grams.*	*Grams.*		
C	As received	3.11	820	272	125	2,880	3,720
C	Aërated 3 months	2.99	820	272	130	1,728	2,982
D	As received	2.99	820	272	135	2,148	3,336
D	Aërated 3 months	2.91	820	272	150	1,104	2,172

The low gravity may be the result of premature caking or partial induration. It is well known that regauged cements harden very slowly. The addition of foreign substances to the cement, such as clay, sand, or slag, produces the same effects. Adulterated Portland cements are seldom met with, but sample B (see table of chemical analyses Appendix 1, Parts 1 and 2) must be considered as such since it contains 11.2 per cent of clay and sand.

Decidedly underburned cements fresh from the kiln may have high specific gravities but such cements seasoned sound have a low specific gravity, a high loss on ignition, and harden slowly. The proof that cements C and D are of this class lies in the fact that it is practically impossible to season good, hard-burned Portland cement clinker to the extent shown by these samples. Furthermore, these cements contained so much free and slaked lime that

which would necessitate the prolonged exposure of the cement in thin, frequently turned layers) to a low gravity and then regrinding it. Such treatment would often increase the efficiency of Portland cement both in sand-carrying capacity and constancy of volume, but it is too expensive to be practical.

the microscopic test revealed an almost transparent field in polarized light due to the presence of a large quantity of calcium hydroxide phenol crystals (Table VIII, Part 1). On the other hand cement G which has the highest specific gravity and shows the greatest strength in both sand and neat, 7- and 28-day mortar tests, was obtained from hard-burned clinker because it requires a well-sintered product to produce a sound Portland cement with a specific gravity as high as 3.11. The comparatively great early strength is the more marked because this cement was rather coarsely ground.

CHARACTERISTICS OF COMMERCIAL PORTLAND CEMENT.

General classification.—These facts concerning the hardening properties of underburned and hard-burned Portland cements enable us fully to designate the character of all commercial cements and to account for the general nature of their hardening properties.

Adulterated, coarsely ground, or caked cements are readily detected by means of chemical or physical examinations. Such products show poor early and ultimate strength.

Underburned cements, when sound, have a low gravity, and microscopic and chemical tests prove whether the low gravity is due to underburning or to excessive seasoning.

If the cement is sound, a high gravity (above 3.10) is positive proof of hard-burning; and we have always found that such high-gravity cements show the characteristic hardening properties of well-sintered Portland cement.

Intermediate products of cement kilns are represented by a specific gravity which is neither high nor low. Such materials usually consist of a mixture of soft- and hard-burned cement, and show no definite character in hardening properties.

Early strength.—The high early strength of Portland cement depends primarily upon the thorough sintering or fusing of the raw materials into desirable compounds of base- and acid-forming metallic oxides. The best commercial practise produces a sound, finely ground product with a low content of volatile constituents and a specific gravity above 3.10. Well-burned cements, if unduly exposed to moisture or atmospheric influences, will deteriorate; not, however, without a lowering of the specific gravity and a correspondingly increased loss by ignition. Therefore, in order to obtain the most desirable material it is necessary to demand perfect soundness, extreme fineness, and a high specific gravity.

Constancy of strength and volume.—Although hard burning is essential to the greatest efficiency in early strength, even some of the hardest-burned Portland cements show considerable fluctuations in strength and volume after they have become thoroughly indurated, and there is no means of ascertaining beforehand how great this ultimate change may be.

The extensive investigations made by a committee of the Society of German Portland Cement Manufacturers failed to establish any definite relationship between the durability of strength and any of the so-called accelerated tests for constancy in volume. Also, the 1-, 7-, and 28-day tests for strength fail to give definite information in this respect. That other methods based upon chemical composition or upon the strength of steamed or boiled mortars have proved equally as unsatisfactory is apparent from the differences in the requirements of the standard cement specifications of various countries intended to control this factor. The British specifications insist upon the Le Chatelier test for constancy in volume and demand specified gains in tensile strength between 7- and 28-day periods; the American specifications only demand no retrogression in similar tests for strength and permit unsoundness in the accelerated test; and the Germans rely almost entirely on the compressive strength of sand mortar cubes and use no accelerated tests. Our results indicate that the fluctuations in the strength of indurated cement were due largely to the same internal strains which developed abnormal changes in volume.

Effects of free lime on the volume of indurated, hard-burned cement.—In most respects the results obtained by measuring the changes in volume of bars of neat and sand mortars verified the previous work and conclusions of E. D. Campbell and A. H. White,[86] who were the first to measure the effects of hard-burned free lime and free magnesia on the volume constancy of Portland cement.

Campbell and White found that bars of neat mortar of nonseasoned, hard-burned Portland cements which apparently contained no free lime seldom showed when immersed in water a linear expansion of more than 0.040 per cent. Bars of similar cement kept in air contracted in volume and in a remarkably uniform manner. The smallest contraction noted at the end of four years was 0.300 per cent and the highest 0.392.

In order to prepare a hard-burned cement containing free lime, these investigators added calcite, crushed and sized to pass a 12- and remain on a 20-mesh sieve, to a normal, raw mixture. In this way they manufactured a hard-burned cement which contained about 2.8 per cent of free lime, the

effect of which is apparent from their results some of which are plotted in the form of expansion curves in fig. 25.

As pointed out by Campbell and White, bar 77A, which had been immersed in water for five years, showed the gradual expansion and the slight drop in the curve at about six months usual with good cements. Bar 78A of the same cement, to which had been added about 2.8 per cent of hard-burned free lime, expanded 0.220 per cent in water during the first week. It continued to expand at a comparatively rapid but diminishing rate until after two months, when the rate of expansion had settled down to practically a normal rate, showing that the free lime had become completely hydrated by two months' immersion in water.

The beneficial effects of aging even a hard-burned, sound cement is shown by the much greater constancy in volume as compared with the fresh cement. However, the aged cements show the customary expansion after three months.

The effect of free lime on cement bars kept in air was not perceptible during the first seven days. The bar of cement containing 2.8 per cent of hard-burned free lime contracted at a normal rate during the first seven days in air, but expansion due to hydration of the lime was noticeable after that date and continued to increase at an accelerated rate until at the end of nine months the bar had expanded 1.17 per cent and had cracked so badly that observations were discontinued.

In case free lime is present in cement used in structures above ground, or where it is usually dry, the expansion will be gradual but several times greater in volume than when the material is under water. The hydration of the hard-burned lime in air is so slow that there may be continuous expansion up to five years or more. Aging diminishes the expansion somewhat, but a cement aged seven weeks when ground still showed the influence of free lime.

In a similar manner the influence of free magnesia was determined. It was found that the rate of hydration of hard-burned magnesia is almost imperceptibly slow, so slow, in fact, that aging does not seem to diminish its deleterious effects and the 24-hour boiling test does not detect it even when as much as 4 per cent hard-burned free magnesia is present. Owing to this slow rate of hydration, hard-burned free magnesia has no appreciable effect in cement used above ground where it is continually dry. Even when continuously immersed in water the expansion due to this constituent is not appreciable until after two months and only becomes distinctly evident after a year. The expansion then continues at an increasingly rapid rate for at least five years.

Campbell and White's observation that any cement worked up fresh will change in volume more than if properly aged and will show a noticeable drop in the curve representing change of volume after about three months, a period which corresponds to that in which briquettes show a falling off in tensile strength, suggested that the fluctuations in strength might be due to the slow hydration of free lime.

In order to gain further information about the slaking of free lime in hard-burned rotary clinker, expansion bars were made of neat mortar using the cements described in Table LII.
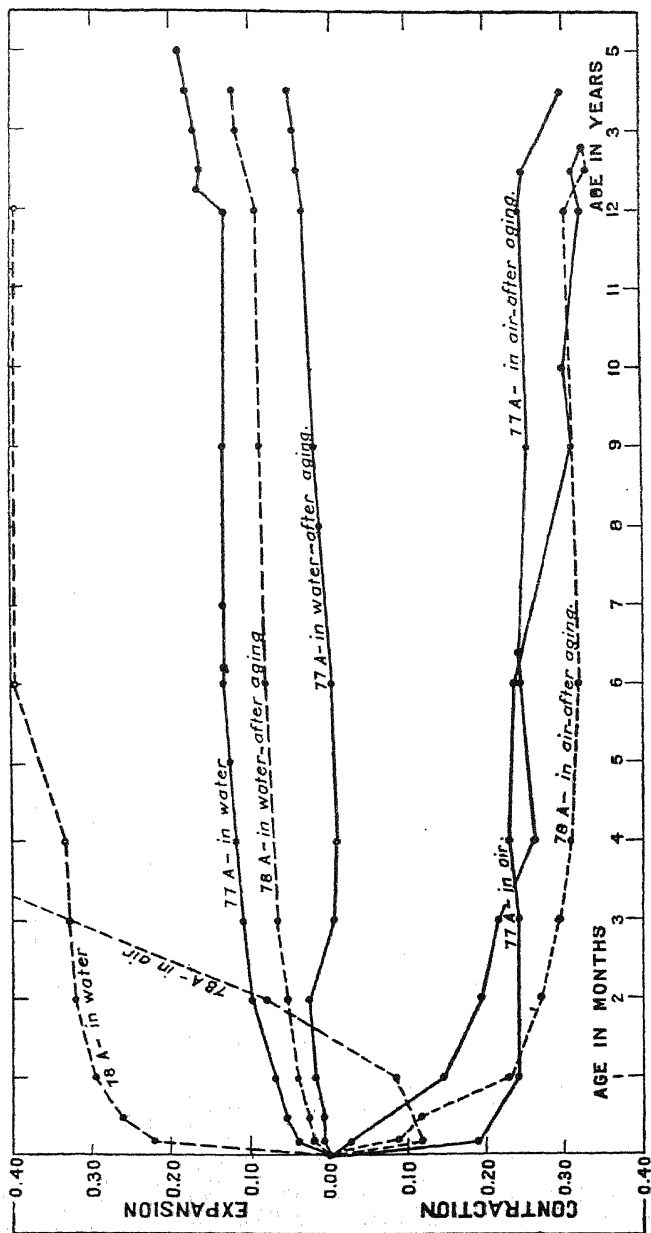
FIG. 26.—Expansion curves showing the effect of free lime in indurated Portland cements made by Campbell and White.

TABLE LII.—*Physical properties of five samples of Brand O cement subjected to tests for constancy of volume.*

No.	Description	Content of plaster.	Specific gravity.	Fineness.		Soundness.		Tensile strength in pounds per square inch.							
				200-mesh.	100-mesh.	5-hour steam test.	After 1 year in water.	Neat mortar.				1:3 Ottawa sand mortar.			
								7 days.	28 days.	3 months.	1 year.	7 days.	28 days.	3 months.	1 year.
		Per ct.		Per ct.	Per ct.										
1	Selected, hard-burned, nonseasoned, rotary clinker containing less free lime than No. 3.	2.5	3.153	91.0	100.0	Sound	Sound	718	784	746	707	296	361	360	320
2	Same as No. 1, but aërated as ground cement 3½ months.	2.5	3.004	91.0	100.0	Disintegrated and soft.	do	482	612	683	652	208	329	397	353
3	Hard-burned, nonseasoned, rotary clinker containing considerable free lime and rather coarsely ground.	2.0	3.145	70.0	88.8	do	do	756	731	721	671	254	253	218	243
4	Same as No. 3, but reground	2.0	3.145	93.8	99.7	Sound	do	X	X	X	X	357	399	364	350
5	Typical sound, hard-burned, rotary, commercial product aërated as clinker 2 months and as ground cement 3½ months.	2.0	2.955	78.0	96.0	do	do	475	556	685	623	194	284	361	338

These bars were submerged in running water and changes in their length were detected and measured with a Bauschinger apparatus. The results obtained are plotted in fig. 26.

The diagram shows that it took from three to seven months' immersion in water to slake the hard-burned free lime in these commercial cements. The free lime in the cement clinker manufactured by Campbell and White existed in particles so coarse that they remained on the 20-mesh sieve, and the subsequent regrinding of this clinker to a fineness passing the 100-mesh sieve left all of the free lime in a very fine and unprotected state. In commercial cements the free lime is less finely ground and more or less protected by coatings of slag which accounts in a measure for its slower hydration. Sample 4 which was reground to pass the 100-mesh sieve, showed no decrease in volume until after seven months thus proving that the free lime in the hard-burned commercial product slaked much less readily than that prepared in the small experimental kiln. The slower slaking of the free lime in commercial products is readily accounted for by the longer time during which the raw-meal is confined in the clinking zone of the kilns.

These results show our general experience that abnormal expansion, like the free lime on which it depends, is not eliminated entirely by a prolonged aëration of either the ground cement or clinker.

Expansion bars made of 1:3 Ottawa sand mortars changed in volume more than was indicated by observations on the neat mortars. Usually the sand mortars changed very little in volume during the early period of hardening, the tendency being to contract unless considerable free lime was present; but after two or three months, expansion took place, due probably to the filling of the voids in the sand mortar. After six or seven months the characteristic contraction was very well defined. Usually, also, the total change in the length of the bars of sand mortar was at least half that of neat mortar. An instance is given in fig. 27 in which the change in volume was even more marked in the sand than in the neat mortar.

The irregularities in the curves of expansion of cement mortars can be attributed to differences in the physical condition of the particles of free lime and to the impermeable nature of indurated neat mortar. The much greater permeability of a 1:3 sand mortar permits the hydration to progress more uniformly than in neat mortars, and, therefore, the results of hydration are more clearly defined in the sand mortars. For the same reason aëration tends to produce more sharply designated changes in volume.

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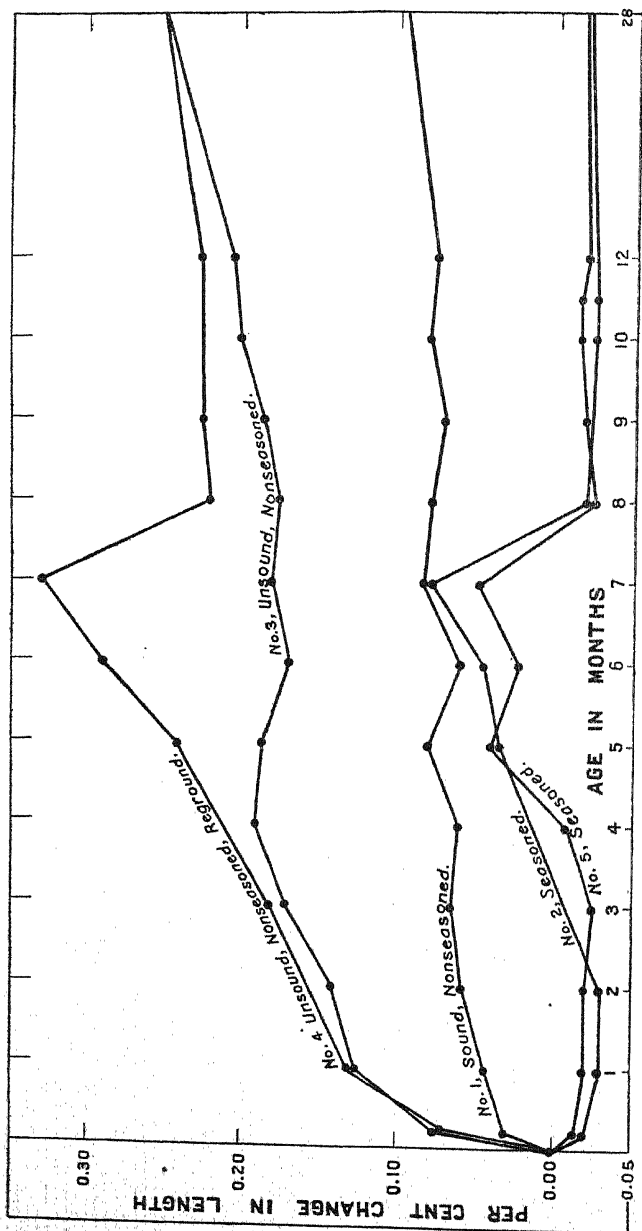
FIG. 26.—Expansion curves showing the effect of free lime in indurated, hard-burned commercial Portland cements submerged in water.
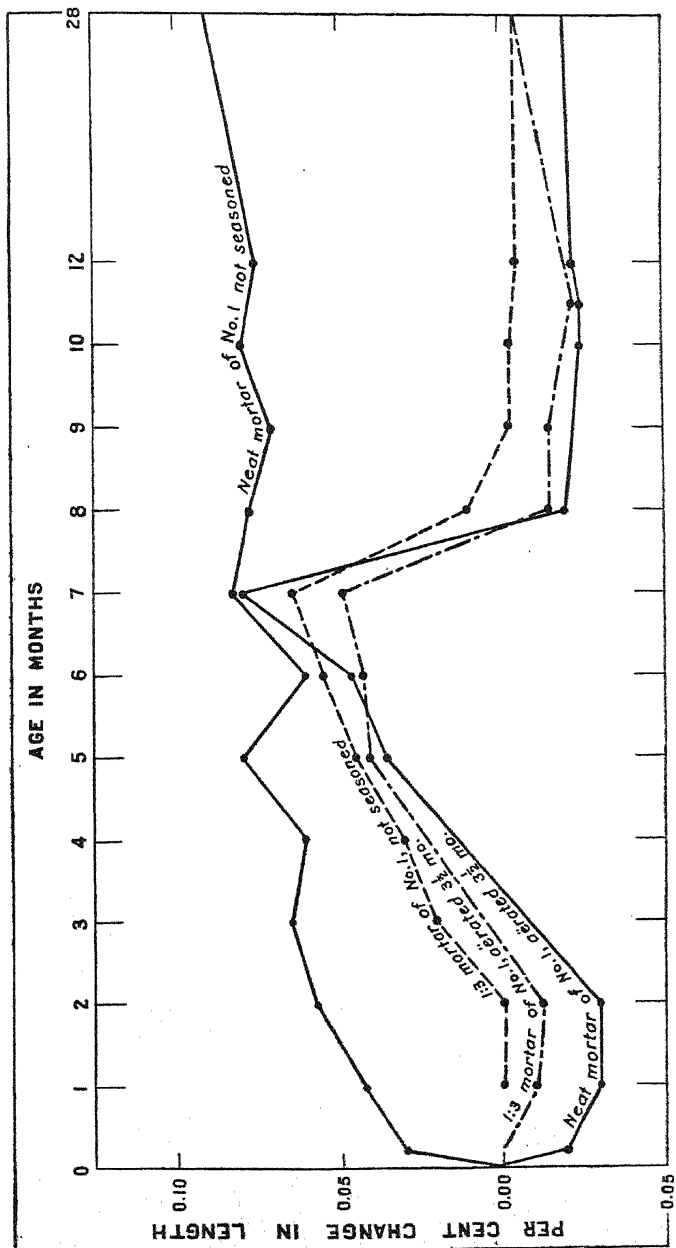
FIG. 27.—Diagram showing the effect of permeability on the expansion due to free lime.

As the free lime in the commercial cements could not be eliminated entirely without greatly reducing the available strength, exact measurements of the loss of strength due to free lime were impossible.   However, contrary to the general belief, our results indicated that a normal Portland cement which contained no free lime would contract in either air or water.   For example, sample 2, Table L, had been aërated as ground cement until it contained no free lime which would react with the phenolate solution. It hardened with considerable rapidity in water, the 7-day briquettes showed 482 and 208, and the 28-day, 612 and 329 pounds for neat and 1:3 sand mortars, respectively.   During the same period of time and for at least a month longer both the neat and sand mortars continued gradually to contract.   Therefore, it seems evident that as long as the free lime remained inert the cement continued both to harden and to contract.

The fact that sound cements even when fresh expand in water offers no contradiction to this belief, because the soundness of the cement does not prove that free lime is absent.   On the other hand all results show that the more perfect the burning of the raw materials into compounds of lime, silica, alumina, and iron, the less will be the expansion of the nonseasoned cement in water. Also, this belief is not contradicted by the established fact that Portland cement mortars and concretes exposed to alternating wet and dry conditions show corresponding expansion and contraction, because the more rapid slaking of the free lime when the material is wet accounts for the changes in volume.

Effect of changes in volume on the strength.—From the action of the nonseasoned samples in Table L and fig. 26, it is evident that hard-burned Portland cements may show a constant gain in strength in spite of considerable expansion.   However, if this expansion is due to the latent slaking of free lime and this action contributes nothing to the strength of the cement, it must tend to weaken the indurated material.   It seems logical to assume that within the limits of perfect elasticity the internal stress due to the slaking of free lime should manifest itself more in the determinations of tensile than of compressive strength.

To test this assumption sample 4, Table L, was aërated as ground cement and tested after three and seven days' exposure. Table LI records the results obtained.

TABLE LI.—*Relative changes in tensile and compressive strength produced by aëration. Cement O, reground.*

Sample No.	Description.	Specific gravity.	Strength of 1:3 Ottawa sand mortar in pounds per square inch.							
			Tensile strength.				Compressive strength.			
			7 days.	28 days.	3 months.	1 year.	7 days.	28 days.	3 months.	1 year.
1	Nonseasoned	3.145	357	399	364	350	3,130	3,160	3,620	3,600
2	Aërated 3 days	3.09	379	417	431	402	2,970	3,265	3,565	4,200
3	Aërated 7 days	3.07	358	454	462	451	2,635	3,765	3,300	4,560

The microscopic test of the cement aërated three days showed very little nonslaked free lime. Owing to the preliminary hydration, its expansion, especially during the early stages of induration, was much less than that of the nonseasoned material, and the early tensile and compressive strengths were increased.

Sample 3 had aërated until most of the slaked lime had been converted into calcium carbonate which accounts for the low strength at seven days. The beneficial results obtained from greater constancy in volume are apparent from the strength developed later.

Apparently there is no direct relationship between the corresponding tensile and compressive strengths during the period of time in which the cements show marked changes in volume. However, at the end of one year, when the volume has become constant and apparently no internal stresses are operating, there is a more or less direct relationship between these factors. Hence, it appears that fluctuations in strength are caused by internal strains which tend to produce changes in volume, and that, within the limits of perfect elasticity, these internal strains affect the strength in tension and in compression in unlike manners.

Numerous instances proved that the internal stresses developed in a contracting mortar do not favor the compressive strength, and that a decrease in volume after an abnormal expansion is very apt to be accompanied by a corresponding decrease in compressive strength even though the tension test shows at the same time an increase in strength.

It has been stated that the beneficial results derived from aëration, as recorded in Table LI, are due to the removal of nonslaked free lime. If this is true, then the early strength

developed by an indurated Portland cement should be the more reliable the less free lime it contains. The results obtained by testing two hard-burned cements, one of which contained more nonslaked free lime than the other, are recorded in Table LII.

TABLE LII.—*Physical properties of hard-burned commercial cements, brands L and O.*

Brand.	As received.[a]	Reground.[a]	Total increase in the length of neat expansion bars kept in water.
			Per cent.
L	A little slaked lime and a little hard-burned, nonslaked lime.	A slight increase in the amount of slaked and nonslaked free lime.	0.044
O	More slaked and nonslaked lime than brand L.	A considerable increase in the amount of slaked and nonslaked free lime.	0.075

| Specific gravity (dried at 110°). | L | 3.11 | | |
| | O | 3.08 | | |

Fineness	L	81.2 per cent through the 200-mesh sieve.
		97.3 per cent through the 100-mesh sieve.
	O	77.4 per cent through the 200-mesh sieve.
		95.2 per cent through the 100-mesh sieve.

[a] Lime determined microscopically by the phenolate test.

The 7- and 28-day results show that cement O had much greater early strength, due in all probability, since L was ground the finer, to its larger content of quick-hardening calcium silicates and aluminates. However, the strength of cement O improved very little with age, showing in many instances even a marked ultimate decrease.

On the other hand, cement L, which contained less free lime and possessed greater constancy in volume, improved considerably with age, the 28-month report showing in all instances, whether constantly submerged in water or weathered outside in the sun and rain, a decidedly greater strength than at seven and twenty-eight days. In spite of its comparatively low early strength, cement L showed the greater efficiency at the end of twenty-eight months.

Tensile and compressive strengths in pounds per square inch.

Ce-ment.	Description.	Age in days.		Age in months.					Per cent of gain based on strength.	
		7.	28.	3.	6.	12.	24.	28.	7 days.	28 days.
L	Tensile strength of neat mortar in water _____	ᵃ509	603	668	703	670	690	666	+ 30.8	+10.4
O	_____do _____	653	707	718	664	641	652	651	− 0.3	− 7.9
L	Compressive strength of neat mortar in water__	4,620	6,100	6,820	7,930	✕	✕	11,010	+138.3	+80.5
O	_____do _____	7,050	8,250	7,550	8,150	✕	✕	9,890	+ 40.3	+19.8
L	Tensile strength of 1:3 Ottawa sand mortar weathered outside_____	239	393	375	455	514	537	763	+219.0	+94.2
O	_____do _____	339	476	380	350	389	547	683	+101.7	+43.5
L	Compressive strength of 1:3 Ottawa sand mortar weathered outside _	2,130	3,130	2,820	4,100	✕	✕	5,260	+147.0	+68.1
O	_____do _____	2,620	3,630	3,780	4,040	✕	✕	4,980	+ 88.2	+35.8
L	Tensile strength of 1:3 Ottawa sand mortar in water _____	233	287	347	369	370	348	345	+ 48.1	+20.2
O	_____do _____	313	379	364	340	304	269	278	− 11.2	−26.7
L	Compressive strength of 1:3 Ottawa sand mortar in water _____	✕	2,030	2,340	2,930	✕	✕	3,280	✕	+61.6
O	_____do _____	✕	2,565	2,660	3,950	✕	✕	3,537	✕	+37.9
L	Tensile strength of 1:3 quartz sand mortar in water_____	153	201	283	280	288	265	255	+ 66.7	+26.8
O	_____do _____	227	297	291	269	234	200	195	− 14.1	−34.4
L	Compressive strength of 1:3 quartz sand mortar in water_____	1,645	2,120	2,160	2,200	✕	✕	2,921	+77.6	+37.7
O	_____do _____	2,187	2,873	3,051	2,727	✕	✕	3,073	+40.8	+ 6.9

ᵃ The value of each test represents the average of 10 determinations.

Therefore, it is evident that greater constancy in volume and strength is obtained by reducing the quantity of free lime in hard-burned Portland cements regardless of whether this is accomplished by seasoning or by better burning.

The same conclusions may be drawn from the data of others.

For example, 7 brands of typical, American rotary cement, the physical properties of which showed that they were all hard-burned products, were examined at the St. Louis Testing Laboratories.[57] Twelve of the 70 samples tested gave imperfect results when subjected to the steam test and, although the unsoundness was slight, the characteristic effect of the

excessive free lime which caused the steamed pats to warp manifest
itself very distinctly upon the strength. This is apparent from the figure
in Table LIII which record the average results obtained from the 1
samples which warped, together with the average of the other 58 soun
samples.

TABLE LIII.—*Average tensile and compressive strengths of typical
American hard-burned Portland cements.*

Mortar.	Cement.	Strength in pounds per square inch.					
		7 days.	360 days.	Gain.	7 days.	360 days.	Gain.
				Per ct.			*Per ct.*
Neat	Sound and unsound	669	696	4.0	5,009	12,028	138.1
	Unsound[a]	709	685	3.4	5,903	12,088	104.7
	Sound	667	698	5.6	4,824	12,016	149.1
1:3 Ottawa sand	Sound and unsound	270	366	35.5	1,117	3,741	234.9
	Unsound	295	365	23.7	1,200	3,660	205
	Sound	265	367	38.3	1,103	3,755	240.4

[a] Samples C. T. 13, 17, 14, 63, 24, 9, 5, 10, 11, 28, 39, 53.

Instances have been noted in which a sound Portland cement
showed as decided a drop in strength as an unsound product,
but as the soundness tests often fail to measure or even to detect
the quantity of free lime or to designate its condition this
apparent discrepancy is readily accounted for. When the condi-
tion and quantity of free lime is determined by means of the
microscopic phenolate test, discrepancies do not occur. We have
found this effect of free lime so characteristic that no 28-day or
longer test is needed to determine the fitness of cements for
use. If an otherwise satisfactory cement hardens in a desirable
manner for about seven days and the microscopic test shows
only a very little hard-burned free lime after this cement has
been reground, then there is no doubt about the ability of the
material to continue to harden in a satisfactory manner for
years. Free magnesia is not detected by the microscopic or
boiling tests, but as the total magnesia is maintained below
5 per cent and its combination with silica and alumina is
dependent upon the same conditions of proper burning as lime,
it is evident that the less the free lime the less also the free
magnesia.

In the hands of an expert the microscopic test for free lime
gives more definite and reliable information regarding the fu-
ture behavior of hard-burned Portland cements than 28-day or

even 3-month tests for strength. The study of a large number of commercial products has convinced us that in a few days we can positively identify those commercial Portland cements which are best suited to our needs.

The effect of the degree of pulverization.—The grains of true Portland cement too coarse to pass a standard 150-mesh sieve are practically inert. The fine impalpable flour, too fine to be measured on any sieve, gives the cement its real adhesive and hardening properties. The coarse, inactive particles may be considered as clinker the finer grinding of which produces a cement whose efficiency depends upon the same conditions of composition, burning, seasoning, etc., as that of the impalpable powder produced from larger clinker in the ordinary process of manufacture.

The only new consideration which the subject of fineness introduces into this investigation is the permanency of the strength developed by the finest and most active particles. A sample of the hard-burned cement L, the physical properties of which are recorded in Table LII, was reground until less than 3 per cent remained on the 200-mesh sieve, and then tested. The results obtained with the original and the reground products are recorded in Tables LIV and LV.

From the data recorded in Table LV the effect of fineness upon the hydration of the hard-burned free lime is noticeable; the characteristic slight decrease in strength after thorough induration occurs more rapidly and disappears more quickly in the reground material. Both the commercial and reground products show the same general characteristics in hardening properties; the ultimate strength of the reground material is so decidedly better than that of the coarser cement that the greater efficiency in the early strength of the former is maintained.

These and other results proved the durable nature of the products formed by the induration of the finest and most active particles of hard-burned Portland cement, and considering the fact that free lime hydrates the more readily and thoroughly the finer its state of subdivision, one can readily explain the great improvement in the commercial product due to the improved degree of final pulverization.

Improved grinding machinery has enabled manufacturers to turn out a finer cement which seasons more efficiently, is more reliable in the tests for constancy in volume and strength, and has increased sand-carrying capacity and better troweling properties. The importance of demanding best commercial grinding

practise is therefore self-evident. However, our present standard specifications permit the manufacture and use of Portland cements which may contain as much as 25 per cent of inert materials, the pulverization of which would add about 20 per cent to the efficiency of the product at an additional cost of less than 5 cents per barrel.

TABLE LIV.—*Physical properties of cement L before and after regrinding.*

Condition.	Specific gravity.	Fineness.		Time of setting.		Soundness (5-hour steam test).
		Through the No. 200 sieve.	Through the No. 100 sieve.	Initial set.	Final set.	
		Per ct.	*Per ct.*	*Hrs. Min.*	*Hrs. Min.*	
As received	3.110	81.2	97.3	2 20	5 0	Sound.
Reground	3.105	97.5	99.9	1 15	3 0	Do.

TABLE LV.—*The effect of fineness upon the temporary and permanent strength of hard-burned Portland cement L.*

Cement.	Description.	Age in days.		Age in months.					Per cent of gain based on strength at—	
		7.	28.	3.	6.	12.	24.	28.	7 days.	28 days.
L	Tensile strength of neat mortar in water	b 509	603	668	703	670	690	666	+ 30.8	+ 10.4
La	do	583	624	655	646	608	640	642	+ 10.1	+ 2.9
L	Compressive strength of neat mortar in water	4,620	6,100	6,820	7,930	×	×	11,010	+138.3	+ 80.5
La	do	5,430	6,480	9,000	10,600	×	×	11,300	+108.0	+ 74.4
L	Tensile strength of 1:3 Ottawa sand mortar weathered outside	239	393	375	455	514	537	763	+219.0	+ 94.2
La	do	287	425	366	444	461	637	792	+175.7	+ 86.4
L	Compressive strength of 1:3 Ottawa sand mortar weathered outside	2,130	3,130	2,820	4,100	×	×	5,260	+147.0	+ 68.1
La	do	1,920	2,900	3,840	5,110	×	×	6,360	+203.1	+119.3
L	Tensile strength of 1:3 quartz sand mortar in water	153	201	283	280	288	265	255	+ 66.7	+ 26.8
La	do	190	287	350	322	289	291	303	+ 59.5	+ 5.6
L	Compressive strength of 1:3 quartz sand mortar in water	1,645	2,120	2,160	2,200	×	×	2,921	+ 77.6	+ 87.7
						×	×			
La	do	1,590	2,490	3,120	3,260	×	×	3,530	+122.0	+ 41.7

a Reground.
b The value of each test represents the average of 10 determinations.

In order to secure the greatest early strength, it is necessary to sinter or fuse the raw materials at a high temperature.

The endurance of great early strength, increases in strength with age, and constancy in volume are the more satisfactory the less free lime or free magnesia the indurated cement contains. This is corroborated by the fact that in the laboratories of many manufacturers it is known that if the material has been burned so that the freshly ground product is sound, tests for strength are not necessary. We believe that the manufacturers should be required to produce a Portland cement which is sound when fresh and which accordingly needs no curing whatever to enable it to pass the hot tests.

In order to secure the formation of desirable quick-hardening compounds and a minimum of free lime, raw materials must be of proper chemical composition, finely ground, very thoroughly mixed, and hard burned. The finished product must be ground to extreme fineness and properly packed. Therefore, efficiency is obtained at a corresponding expense to the manufacturer, and cements should be purchased on a basis of quality rather than upon a mere consideration of quantity.

PART I. FREE LIME IN PORTLAND CEMENT.

(1) A method for determining the approximate amount of free lime and for distinguishing between sintered, nonsintered, and slaked lime is described.

(2) The application of this test gave conclusive proofs of the presence and the effects of free lime in all the commercial Portland cements examined, and a study of this free lime under different conditions of burning, grinding, and seasoning showed the following results:

A. The degree of burning:
   (a) As the kiln temperature increases, nonsintered calcium oxide gradually becomes converted into a sintered state having different physical properties.
   (b) This conversion may occur at temperatures far below those necessary for the proper burning of the cement.
   (c) Underburned cement may contain both sintered and nonsintered lime.
   (d) All the free lime in hard-burned cement is sintered.
   (e) Portland cement clinker can be burned perfectly so as neither to contain free lime nor to have lime liberated in the ordinary process of cooling and grinding.

B. The effects of seasoning:
   (a) Nonsintered lime hydrates more easily than sintered lime.
   (b) Sintered lime may hydrate so slowly by mere exposure to the atmosphere that the action is largely confined to the outer exposed parts of the particles and only gradually penetrates to their interior.
   (c) The penetration of air into a mass of ground cement is limited approximately to a thin outer layer.
   (d) When cement is aërated in thin layers, the conversion into carbonate goes on practically as fast as hydration.
   (e) The aëration tends to coat the particles of sintered lime with an impermeable film of calcium carbonate so that even thoroughly aërated, finely-ground cement may contain unslaked free lime.

C. The effect of free lime upon the soundness:
   (a) The usual cause of unsoundness is unslaked free lime.

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(b) The effect of free lime upon the soundness is influenced by the cohesive properties of the cement, the "speed of slaking," the fineness, the temperature, the amount of water used in gauging, and the effect of impurities and retarders.

(c) The test for soundness as an indication of the presence of free lime is relatively crude compared with the microscopic study of calcium hydroxide-phenol crystals.

(d) Slaked lime does not cause failure in soundness tests.

(e) Nonsintered lime must be present in quantity to cause unsoundness, in which case the disruption is likely to occur in water or air, as well as in steamed pats.

(f) Fused sintered lime is liable to cause unsoundness in the accelerated tests.

(g) The agreement between the microscopic evidence of free lime and the result of tests for soundness was very close.

PART II. THE SEASONING OF PORTLAND CEMENT.

(3) The absorption of both gaseous substances by both clinkers and pulverized cement verified the microscopic tests and demonstrated the following:

(a) The penetration of air into a mass of undisturbed cement is less than 13 millimeters. Water absorbed from the atmosphere may slowly penetrate farther.

(b) Cements stored in air-tight receptacles show a slow decrease in the percentage of moisture, due, as evinced by the microscopic evidence, to the slaking of free lime.

(c) The rate of absorption decreases very rapidly as the reaction proceeds, and the fine particles absorb proportionally more than coarser ones.

(d) Under the same atmospheric conditions the amount and rapidity of absorption depends largely upon the quality and quantity of free lime.

(e) Perfectly sintered clinker is practically inert to water and atmospheric influence and consequently the free lime embedded in this hard, dense, inert magma is more thoroughly protected than the free lime in underburned clinker, and hard-burned clinker may season less efficiently than soft-burned clinker.

(4) A study of manufacturing practises and the strength developed by hard-burned and underburned cements led to the following conclusions:

(a) Aëration is the least efficient practical method of seasoning Portland cement.

(b) A high loss by ignition and a corresponding low specific gravity are not characteristic of commercial cements made from well-burned clinker.

(c) Cement made entirely from underburned clinker seldom appears on the market except as hydraulic lime, because it would fail to pass the test for strength. Underburned cement usually comes to the consumer mixed with the harder-burned material from the same mill and the present specifications of the American Society for Testing Materials are such that a mixture of 45 per cent of disintegrated clinker and 55 per cent of sound clinker passed all requirements except the percentage loss by ignition. This emphasizes the great value of the test for volatile constituents.

(d) The best set-kiln process yields a considerable amount of under-burned clinker which, if not removed, does not give a true Portland cement but a mixture of seasoned underburned and well-burned cement containing sintered, nonsintered, and hy-drated free lime, calcium carbonate, etc.

(e) The rotary kiln is capable of producing a more uniformly burned clinker than the set kiln. Extreme fineness in the grinding of the raw material is necessary to produce a perfectly sintered product. Few manufacturers grind finely enough. The ma-jority produce a hard-burned clinker which still contains a considerable percentage of free lime some of which fails to slake before induration and causes the much-discussed charac-teristic drop in the strength of rotary cements.

PART III.   THE SETTING PROPERTIES OF PORTLAND CEMENT.

(5) For determining the time of initial and final set, the method employing the Vicat needle was found to be reliable, impartial, and accurate, and abnormal results were obtained only with cements of very poor quality.

(6) Preliminary experiments on the setting properties of com-mercial products demonstrated the following:

(a) Although cements of different chemical composition have dif-ferent natural setting tendencies, changes in the setting proper-ties are due primarily to the absorption of water or water and carbon dioxide.

(b) Changes in the setting properties were independent of the ulti-mate chemical composition, the fineness, the amount of retarder, the quantity of water and carbon dioxide absorbed, the nature of the raw materials used, or the burning process employed.

(c) Changes in the rate of set are brought about largely by alterations in the condition of the free lime.

(7) Large quantities of fresh, nonseasoned clinkers with char-acteristically different chemical and physical properties were studied and the following results were obtained:

A. Nonseasoned, nonplastered cements:

(a) Manipulated in the ordinary way, the plasticity is poor, and the set abnormal and apparently slow and erratic.

(b) The set takes place so quickly that the cements become regauged by any ordinary process of manipulation.

(c) The immediate generation of heat when water is added is due partly to the hydration of free lime and partly to the setting of the cement.

B. The effects of plaster on nonseasoned cement:

(a) As the amount of plaster used is increased, the initial set takes place earlier, then later, and finally again earlier. The amount of water required for normal consistency at first decidedly decreases, and then slightly increases. The same quantity of plaster does not affect the set and plasticity of different cements to the same extent.

(b) Small amounts of plaster have no appreciable effect upon the slaking of ignited lime, and do not prevent the generation of heat due to the slaking of the free lime.

(c) The effect of minute quantities of plaster is to quicken the set of a manipulated cement until the amount added is sufficient to prevent regauging.

(d) Further additions of plaster retard the set, and from 1.5 to 3 per cent produces a maximum effect. Beyond this amount the natural tendency of plaster of Paris to set quickly manifests itself in the combined results obtained, and the time of initial set again approaches a minimum.

C. The effects of various methods of seasoning the nonplastered, ground cement or clinker:

(a) As soon as the free lime has become thoroughly hydrated, less water and less plaster are required to produce a normal paste of standard consistency and set.

(b) The efficiency of the different methods of seasoning depends entirely upon the relative amounts of calcium hydrate produced and maintained.

(c) The conversion into carbonate decreases the plasticity and the retarding influence of the sulphate.

D. The effects produced by seasoning plastered cements showed that:

(a) No radical difference is manifested if plaster is added before or after the cement has seasoned.

(b) The constituents of the atmosphere may alter the condition of free lime without affecting the compounds which cause cements to set.

(c) The substitution of calcium carbonate for slaked lime reduces the plasticity and decreases the efficiency of plaster or gypsum as a retarder.

(d) Cement itself may finally become practically inert after prolonged exposure.

E. Effect of free lime on retarders:

(a) When free calcium oxide is present, the heat of hydration when water is added increases the natural rate of set. In different cements the normal rate of the setting reactions vary and are not affected to the same extent by heat or retarders.

(b) A preliminary hydration of the free lime adds to the efficiency of the retarder and increases the plasticity.

(8) The following changes which account for all the variations met with in the action of a commercial Portland cement may occur in the rate of set and in the plasticity, namely:

1. An acceleration of the set and an increase in plasticity as regauging is eliminated with the first slaking of free lime.

2. A retardation of the set and a further increase in plasticity with the further slaking of free lime.

3. An acceleration of the set and a decrease in plasticity as the slaked lime is diminished by conversion into calcium carbonate.

4. A retardation of the set and a further decrease in plasticity as the cement tends to become inert after prolonged exposure.

(9) The practical control of the setting properties:

(*a*) An analysis, such as is outlined, of the cement before it is packed is an accurate means of ascertaining the possible effects of storage on the setting properties. It will inform the manufacturer if the set of the product of his kiln is capable of being kept within desirable limits during storage, and will indicate the amount of retarder required.

(*b*) Sometimes a cement must be seasoned before its set can be controlled; but in most instances this is not necessary, and in all instances the necessity for seasoning can be avoided by proper burning.

(*c*) The manufacturer must give special consideration to the effects of hydration of the free lime and not to its conversions into carbonate.

(*d*) Proper packing is necessary for best results.

(*e*) Almost all commercial cements, which failed to pass standard specifications on account of their rate of set, would have proved satisfactory had they been seasoned or plastered properly.

(10) A study of the influence of fineness upon the rate of set shows that it requires only the use of a small additional quantity of retarder to overcome this influence, and, with few exceptions, it is certain that manufacturers can control the set of their product even though it is all ground to an impalpable powder.

(11) Special attention is directed to the following results:.

(*a*) Manufacturers especially should give the subject of partial regauging due consideration, in order to avoid shipping cements which, although apparently slow setting at the mill, are apt to be quick setting when tested at their destination.

(*b*) The policy of using a minimum amount of gypsum has often resulted in quick setting material where 0.5 per cent of additional retarder would have prevented all trouble.

(*c*) Exception is taken to the deductions of Conover that quick cooling of the clinker slows the set of the finished product.

(d) Adequate reasons are given for the beneficial results obtained by Bamber's method of grinding the clinker in the presence of a limited amount of live steam. It is suggested that even greater efficiency might be obtained by dropping the red-hot clinker into water as soon as it leaves the rotary kiln.

PART IV.   THE STRENGTH OF PORTLAND CEMENT.

(12) Observations obtained from testing the strength of Portland cement:

(a) High testing rotary cements would meet with universal approval and the problem of cement testing and standardization would be greatly simplified were it not for their characteristic drop in tensile strength.

(b) The failure to establish a more definite relationship between the tensile and compressive strengths can be attributed partly to the fact that the large cubes or cylinders usually used for testing the strength under compression are less apt to show the peculiarities of cement than the small briquettes used for tension test.

(c) Results obtained by crushing small specimens show the up and down values common to tension test curves, but even when all specimens are practically the same size, the values do not always go up and down coincidently.

(d) Tension tests are as useful as determinations of compressive strengths, and a retrogression in the value of either occurs only when due to the development of undesirable, contending influences.

(e) The characteristic fluctuations in strength could not be attributed to the different rates of hardening of the different constituents of the cement and to a deterioration of the sulphates and aluminates.

(f) The development and the maintenance of the early strength does not depend upon the early gain in strength, upon a narrow limitation of the percentage of calcium oxide, the value of the silica-alumina ratio, the hydraulic modulus, nor upon any other available chemical information.

(g) In most instances it was found possible to change the natural effect of any of these factors by altering the degree of burning, the fineness of either the raw material or the finished product, and by seasoning the cement or the clinker in a different manner or to a different extent.

(h) No reliance can be placed on rules which are deduced simply from analyses or percentage of gain.

(13) The physical and chemical properties of free and combined calcium oxides and their influence on the development of the strength of calcareous cements.

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A. The effects of anhydrous free lime:

    (a) Lime which fails to slake before the cement has set is the usual cause of disintegration or weakness.

    (b) Lime burned at a white heat hydrates much more slowly and expands approximately 50 per cent more than lime burned at a low heat.

    (c) Owing to the impermeable nature of indurated neat cement, the expansion due to free lime will not develop equally in specimens of different shape, size, volume, or density.

    (d) The expansive force manifests itself less in lean than in rich mortars and the action of free lime is rendered less harmful by using sands containing pozzuolana.

    (e) When cement is submerged in cold water "this disruptive force may not develop its full value in a month or a year."

    (f) In air, sintered lime slakes much more slowly than in water.

    (g) Owing to the impermeable coating of slag and calcium carbonate, boiling water may fail immediately to attack the free lime in aërated cement unless it has been ground to extreme fineness.

    (h) The force which operates to cause cements and mortars to disintegrate does not become apparent to the eye until it has overcome the strength of cohesion developed by other constituents in the cement.

    (i) If anhydrous free lime is present in a hardened cement and is allowed to slake, it will weaken the latter.

B. The effects of slaked lime:

    (a) Its influence upon the strength depends upon the nature of the cement, and the manner in which it is used.

    (b) Slaked lime does not possess the ability to harden in water, but hydraulicity may be slowly imparted to it by the presence of pulverized pozzuolana.

    (c) If permitted to absorb carbon dioxide, it has cementive properties of its own, but the process of induration is slow and confined more or less to exposed surfaces.

    (d) The presence of slaked lime may affect the strength of a cement in a mechanical manner, because it shrinks very much if permitted to dry, increases the plasticity, and in certain conditions decreases the permeability.

C. The effects upon the strength of various combinations of calcium oxide with silica, alumina, or iron oxide:

    (a) The pulverized, fused, or perfectly sintered calcium compounds in calcareous cements possess the property of hardening under water, without an appreciable change in volume and without the necessity of preliminary curing.

    (b) With proper mixtures, the nearer we approach a thoroughly combined and fused clinker, the less the expansion of the resulting cement.

(c) Since with the silicates the strength increases as the lime increases while with the aluminates the opposite is true, and since the high silicates and the low aluminates require the greater heat, it follows that the strongest cements require the highest burning temperatures.

(d) The differences in the physical properties of the various calcium compounds account for the failure of ultimate chemical analyses to reveal the true nature of commercial cements.

(e) Combined magnesia like combined lime has no injurious effect in cement.

(f) The hardening process of hydraulic calcium compounds is to a large extent not limited to exposed surfaces, but takes place throughout the mass, which is one of the reasons that good Portland cements give more constant and reliable results than other calcareous cements.

(14) The effects of the condition of free and combined lime in hydraulic cements:

(a) From the natural pozzuolane cements, with their low gravity and slow, unreliable hardening properties, there is a rise in efficiency and usefulness through hydraulic lime, slag, and natural cements to the great and reliable strength of good Portland cement, solely by reason of the condition of the free and combined lime content.

(b) Overburned natural cement is essentially underburned Portland cement, and the evil effects resulting from either process are due to the production of a maximum amount of slow slaking, sintered free lime, and free magnesia.

(c) A more efficient natural (or Roman) cement than that produced at present by burning cement rock in set-kilns could be manufactured by blending clay and limestones in proper proportion and then burning the mixture at a slow temperature in a rotary kiln.

(d) Rapid cooling is an essential to the efficiency of slag cement.

(e) Rapid cooling is not essential to the preservation of high limed silicates and low limed aluminates in Portland cement.

(f) Owing to the unequal degree of burning to which the raw material in different parts of the set kiln is subjected and to fuel contamination, the aggregate produced by this process usually consists of a mixture of all five classes of hydraulic cements in which the well-sintered Portland cement clinker, typical of good rotary practise, predominates.

(g) The characteristic low early strength of set-kiln cement is due to the presence of the underburned material and not to the slow cooling of the clinker.

(h) Portland cements so bad as utterly to disintegrate when subjected to the normal tests for soundness need no further consideration until additional seasoning enables them to remain sound in cold water or air.

(15) The effects of seasoning on the hardening properties of Portland cements:

A. Cement produced from soft, decidedly underburned Portland clinker:
  - (a) Nonseasoned, underburned Portland cement is unsound.
  - (b) Underburned clinker seasons readily.
  - (c) Seasoned to soundness, it hardens very slowly, but shows a steady increase for an apparently indefinite length of time.
  - (d) Ordinarily, expansion due to free lime occurs before or soon after the set, and, therefore, if the percentage of magnesia is low, it is safe to assume the ultimate soundness if the neat mortar does not disintegrate after the usual tests.

B. Hard-burned Portland cements:
  - (a) The hard-burned clinker may, or may not, produce a cement which requires no curing to enable it to pass the accelerated test for soundness.
  - (b) Seasoned or nonseasoned, provided the cement passes the hot tests, it may be used with reasonable certainty of its ultimate soundness; no reliance can be placed on the normal 28-day tests for strength or soundness—facts which ought to be sufficient cause for the rejection of all Portland cements which fail to pass the hot tests.
  - (c) Under normal conditions the expansion due to free lime in indurated cement develops so slowly that it may not effect the early strength.
  - (d) The cement hardens very rapidly and attains a great early strength, but unlike the soft-burned product the strength at the end of years is usually less than at the end of twenty-eight or sometimes even seven days.

C. Sound commercial Portland cements:
  - (a) The early strength of even hard-burned cements can be reduced to a low figure by thoroughly aërating the ground product.
  - (b) Prolonged aëration of the ground product has no marked effect on the ultimate strength of hard-burned cement.
  - (c) Aëration results in the conversion of slaked lime into calcium carbonate, and the tendency of this reaction to confine itself to the surfaces of the individual particles of cement accounts for the manner in which the hydraulic properties are retarded rather than eliminated.
  - (d) Owing to this coating of carbonate, the rate of induration of the inner active constituents of aërated cement depends upon the permeability and exposure of the mortar.
  - (e) The original hardening properties of an aërated, hard-burned cement are restored almost entirely by regrinding; but, although such treatment tends to increase the efficiency both in sand-carrying capacity and in constancy of strength and volume, it is too expensive to be practical.

(f) The characteristic drop in strength may not be eliminated even by prolonged aëration.

(g) The strength and even the character of the curve of strength of any given cement may be affected to a considerable extent by the method of molding employed, the quality of water or of sand used, and the exposure or seasoning resorted to, but in spite of these variable factors certain properties influence the strength to such an extent as to be readily apparent.

(h) A low early strength always results from premature partial regauging or caking; coarse grinding; the presence, in quantity, of foreign substances such as clay, sand, or slag; underburning; or excessive seasoning.

(i) A low early strength, provided the cause is not due to coarse grinding, is always associated with a low specific gravity (dried at 110°) and a corresponding high loss on ignition.

(16) The general character of the commercial cements examined and the general nature of their curves of strength:

(a) Adulterated, coarsely ground or caked cements were readily detected by means of chemical or physical examinations. Such cements showed poor early and ultimate strength.

(b) Underburned cements when sound have a low gravity, and the microscopic and chemical examination in most instances proved that the low gravity was due to underburning rather than to adulteration or excessive aëration. Such material hardened in the manner characteristic of seasoned, underburned Portland cement.

(c) If the cement was sound, a gravity above 3.10 was positive proof of hard-burning, and such material always showed the characteristic hardening properties of a well-sintered Portland cement.

(d) Intermediate products of the cement kilns were represented by a specific gravity which was neither high nor low. They consisted of a mixture of soft- and hard-burned cement and showed no definite hardening properties.

(17) A résumé of the above facts and conclusions proved that hard-burning is essential to the greatest efficiency in early strength and that in order to secure the desired permanency in strength, the destructive force which apparently operates after hard-burned cements have become thoroughly indurated must be discovered and eliminated.

(18) The effects of changes in volume on the strength of hard-burned Portland cements:

(a) Internal strains result from the presence of free lime in indurated cement.

(b) Portland cements expand very little in water unless they contain free lime (or free magnesia).

(c) Within the limits of perfect elasticity, Portland cements may show a gain in strength in spite of considerable expansion.

(d) The strength can be increased by reducing the expansion.

(e) There is no direct relationship between tensile and compressive strengths during the time in which the cements show marked changes in volume.

(f) There is a marked relationship between the strength in tension and in compression after the volume has become constant and apparently no internal stresses are operating.

(g) Fluctuations in strength are caused by internal strains resulting from the hydration of free lime, and within the elastic limit these internal strains affect the strength in tension and in compression in a dissimilar manner.

(h) The early strength, as an indication of the ultimate strength, is the more reliable the less free lime the material contains.

(i) There is definite relationship between the durability of strength and the results of accelerated tests of hard-burned Portland cement.

(j) As the soundness test fails to measure and often even to detect free lime or to designate its condition, the microscopic test offers much more reliable information on this point.

(k) We have found this effect of free lime so characteristic that no 28-day, or longer, test of strength is needed to determine the fitness of cements for use. The study of a large number of commercial products has convinced us that we can ascertain by this means the true quality of Portland cements without resorting to the prolonged tests for strength.

(19) The only new consideration which the subject of fineness introduces is concerned with the permanency of the strength developed by the finest and most active particles. The results obtained proved the durable nature of the indurated impalpable powder, and considering that free lime hydrates more readily the finer its state of subdivision, the great benefits derived from commercial fine grinding are apparent.

(20) Temporary and ultimate strength:

(a) For greatest temporary efficiency it is necessary to grind finely and to burn at a high temperature.

(b) The endurance of early strength, the increase in strength with age, and the constancy in volume are greater the less free lime (or magnesia) the indurated cement contains.

(c) Portland cement of the desired quality can be obtained by proper mixing, hard-burning, and fine grinding.

(d) Cements should be purchased on a basis of quality rather than upon a mere consideration of quantity.

CONCLUSIONS.

(1) The qualities in Portland cement which we need are constancy in volume and setting properties, and reliability of strength, and it is of vital importance that this material both harden rapidly and maintain great strength. We believe that the enforcement of the following recommendations will increase the efficiency of the present standard cement specifications of the American Society for Testing Materials.

A. Concerning the constancy of volume:
  - (a) In order to secure the desired efficiency in Portland cement, the manufacturer must be induced to burn his materials so that no seasoning is required to produce a sound cement.
  - (b) Failure to meet the requirements of the accelerated tests shall (in place of "need not" as now specified) be sufficient cause for rejection.

B. Concerning the specific gravity:
  - (a) In order to secure the best burning and proper storing, the specific gravity of the cement as received (i. e., dried but not ignited) shall not be less than 3.10 unless the loss by ignition is less than 2 per cent.[88]
  - (b) The clause "Should the test of cement as received fall below this requirement a second test may be made upon a sample ignited at a low red heat" should be omitted.
  - (c) The clause "A low specific gravity in conjunction with a high loss by ignition is positive proof of undesirable burning, adulteration, or seasoning" should be substituted for the present paragraphs concerning the significance of the specific gravity.

C. Concerning the fineness:
  - (a) As the specifications now stand, there is little incentive to induce the manufacturer to grind to the degree of pulverization that modern improvements in grinding machinery has made practicable unless his cement is so poor that extreme fineness is necessary to enable it to pass the requirements for strength and soundness. Therefore:
  - (b) That the cement shall leave a residue of not more than 5 per cent by weight on the No. 100, and not more than 20 per cent on the No. 200 sieve.

[88] The above recommendation provides for the possibility of a well-burned cement with a lower specific gravity provided the low gravity is not due to subsequent absorption of volatile constituents; but our experience does not include such a possibility.

D. Concerning the tensile strength:

    (a) That the average of at least four briquettes representing at least two separate mixtures of the same sample shall be taken for each test, excluding any results which are manifestly faulty.

E. Concerning retests:

    (a) Manufacturers should be impressed with the fact that these are minimum requirements; that ample provision already has been made in the specifications for lack of uniformity in testing as well as in real quality; and that a quality so superior should be demanded that, regardless of the variable factors, the ability of cement to pass all requirements shall be a certainty. Therefore;

    (b) The results obtained from the original test shall be considered as final unless it becomes evident that serious error in sampling or testing has resulted in totally misrepresenting the quality of the cement. In other words, that "border-line" cements should be avoided as much as possible.

F. Concerning the practical significance of the above recommendations:

    (a) Manufacturing conditions are such that we can not hope to secure Portland cement which contains no free lime. Also, it is realized that the proposed specifications are not perfect. However, we believe that the enforcement of the above recommendations will support and promote the best practise in grinding and burning, and, accordingly, secure greater uniformity and efficiency than the present specifications.

    (b) Without the hearty, honest coöperation of both manufacturer and user little can be accomplished. The degree of fineness and burning are important financial considerations to the manufacturer, and the consumer should buy on a basis of quality.

    (c) The testing of a great number of commercial Portland cements from many parts of the world has convinced us of the feasibility of these recommendations from both economic and practical standpoints, and the results obtained have disproved all claims to the contrary. For instance, a certain manufacturer in America stated that owing to a long sea voyage he could not guarantee his cement to pass the 3.10 requirement for specific gravity. Our work showed conclusively that cement stored in good barrels undergoes very little change due to atmospheric influences and many cements imported from Europe and America show consistently a gravity above 3.10 and a low loss by ignition. These are the cements which, as stated in the Introduction of our work, show the most remarkable uniformity in physical properties.

(2) We desire to emphasize the importance of the calcium hydroxidephenol microscopic test for free lime, as in every instance

the physical and chemical properties of the different products examined demonstrated the accuracy and usefulness of this test. As stated, we believe that in the hands of an expert it gives more definite and reliable information regarding the constancy of strength and volume than the usual 28-day or even 3- or 6-month tests. However, there is one undesirable feature to this test; namely, that it requires considerable experience and ability correctly to interpret the significance of the phenolate crystals formed on the microscopic slide. Therefore, in order to make this test generally practicable and universally dependable, it must be simplified or made quantitative. Certainly, its possibilities and importance warrant much more extended research in this direction than we have had opportunity to accomplish.

ILLUSTRATIONS.

Fig. 1.   Effect of sun and rain on a cement.

Fig. 2.   The same cement more finely ground.

PLATE VII.

PHILIPPINE GUANO.

By Alvin J. Cox.

(*From the Laboratory of General, Inorganic and Physical Chemistry, Bureau of Science, Manila, P. I.*)

In any agricultural undertaking the total composition of the soil must always ultimately be taken into account, for from the soil under normal conditions certain elements of plant food are derived. Some constituents become exhausted after years of cultivation and the soil requires fertilization in order to make it productive. This is especially true of the elements nitrogen, phosphorus, and potassium. When the percentage of any one of the elements of plant food existing in the solid falls below 0.1, the productive capacity may be questioned. Up to the present time there has been very little fertilizer used in the Philippine Islands. In some places the soil has been seriously exhausted by years of cultivation, and its productivity can not be restored without fertilization.

The maintenance of the productive capacity of soils has been a subject of the greatest concern and interest from the earliest historic times, but the use of commercial fertilizers is not old. Sodium nitrate was first imported into England about 1830 and natural guano ten years later.

With the agricultural development of the Philippine Archipelago the attention of the agriculturist and scientist has been turned to the subject of fertilizers, and it may be of interest to discuss the question of Philippine natural fertilizers—the phosphatic guanos of the Islands. These consist of the excreta of sea fowls and other birds, bats, and marine animals, with more or less bone and animal matter furnished by dead bodies, and are found in large quantities in some places, mainly on small islands and in numerous limestone caves. That from caves is usually bat excrement. Deposits of bat guano have been discovered on a great many of the islands, chief among which are Marinduque, Guimaras, Luzon, and Mindoro; and some of these have been located and recorded. The deposits in some of the caves are reported to consist of one or more thousands of tons. Probably as yet not over 1,000 tons of guano have been mined in the whole Archipelago. In a few instances considerable quantities of bat guano have been removed from church towers.

Guano is somewhat granular in appearance and is usually a brown or grayish powder, but the color varies so much that it

often requires an experienced eye to recognize it. Sometimes when mixed with a small quantity of sand it will be unnoticed by the ordinary observer. In nearly every cave in the Philippines the dirty granular solid on the floor, varying from a few centimeters to a meter or more in depth, is bat guano. Chemical analyses do not distinguish between different kinds of guano. The principal fertilizer ingredients of guano are nitrogen, phosphoric anhydride, potash, and organic matter. Aside from moisture and organic matter, nitrogen and phosphoric anhydride are the most abundant constituents. The composition of Philippine guano is shown by the following more or less complete analyses of the Bureau of Science.

TABLE I.—*Chemical analyses of Philippine guanos.*

Laboratory No.	Date.	Source and remarks.	Moisture (H₂O).	Nitrogen.	Nitrogen as ammonia (NH₃).	Phosphoric acid (P₂O₅).			Total potash (K₂O) except as indicated.
						Total.	Water soluble.	Citrate soluble.	
1007	1903	Unknown; bat guano	24.14	7.28	1.36		0.20		0.91
1030	1903	____do____	33.63	6.47	0.6		0.10		0.50
2498	1904	Mining Bureau sample No. 18-6		8.51		4.28			
1422	July 28, 1903	Cave on Guimaras Island		1.43		12.50	2.30	4.80	1.53
5846	Oct. 31, 1904	Unknown (fine)		2.48		7.11			
5846	____do____	Unknown (coarse)		3.68		6.67			
5950	July 1, 1904	World's Fair exhibit (large pieces)		0.59		8.52			
5950	____do____	World's Fair exhibit (fine)		3.12		4.25			
7030	____do____	Montalban cave	9.54	2.01		7.68			
11034	June 17, 1904	Caves in Batangas		8.51		4.28			
11136	July 14, 1904	Unknown	15.35	8.64		2.53			
13026	Oct. 1, 1904	Bat guano from caves near Pilar, Capiz (surface)		2.13		4.07			
13026	____do____	Bat guano from caves near Pilar, Capiz (1 meter under surface)		1.72		7.58			
14016		Unknown		4.25		4.00			trace
16710	Mar. 15, 1905	Bat guano removed from the roof of a small schoolhouse in San Francisco de Malabon, Cavite	9.20	8.81		5.32	2.26	1.60	0.97
4339		Near Calapan	9.30	2.26		7.31			0.67
4341		____do____	7.63	1.55		1.58			0.65
23654	Oct. 17, 1905	Unknown	42.26	6.70		2.40			
27918	Feb. 14, 1905	____doª____	6.60	0.10		3.93	0.98	2.39	9.10
32476	June 27, 1906	____do____		7.40		5.78			2.46
35701	Aug. 29, 1906	Same as 23654		6.62		2.80			

ª This sample contained 32.77 per cent carbon.

TABLE I.—*Chemical analyses of Philippine guanos*—Continued.

Laboratory. No.	Date.	Source and remaarks.	Moisture.	Nitrogen.	Nitrogen as ammonia (H₂O)	Phosphoric acid (P₂O₅).			Total potash (K₂O) except as indicated.
						Total.	Water soluble.	Citrate soluble.	
36845	Oct. 19, 1906	Unknown	^{b}44.11	0.3		3.17			
38837	Dec. 10, 1906	----do----	14.67		9.58			2.68	2.55
38801	Dec. 14, 1906	Cave on Guimaras Island said to contain 2,000 tons	^{b}60.78		1.79			1.75	0.98
38843	Dec. 27, 1906	Unknown	23.71		0.88			0.90	0.19
39439	Jan. 15, 1907		43.55		0.28			2.31	0.05
39446	Jan. 14, 1907	Mindoro	7.80		1.03			1.40	0.10
39738	Jan. 23, 1907	Unknown; 2 samples	{ 8.64		8.45				2.45
			{ 11.17		9.93				0.15
40685	Feb. 18, 1907	Unknown	68.45		2.17			1.75	^{c}trace
41375		Unknown; 2 samples	{ 18.81		3.10			4.08	^{c}0.58
			{ 18.50		1.08			2.70	^{c}0.09
41616	Mar. 15, 1907	Unknown	8.42		1.12			2.85	1.93
42730	Apr. 13, 1907	----do----	24.98		1.15			0.37	^{c}0.23
42730	----do----	----do----	24.72		0.23			1.70	^{c}0.36
49403	Sept. 19, 1907	----do----	23.62		1.27			3.98	^{c}0.10
43531		----do----	6.4		2.31			4.92	^{c}0.26
44049		Mina Caridad, Monte Luboc, Montalban, Rizal	23.2		5.58			3.76	^{c}0.26
48121	July 26, 1907	Cave on Island of Kapuluan, Tayabas	45.40		0.22	6.05		0.18	^{c}0.02
44083	May 15, 1907	Same as 44049	23.1		2.89	8.56			^{c}0.13
48314	Sept. 2, 1907	Division of mines, Bureau of Science	12.95		3.49			4.69	^{c}0.19
48505	Sept. 5, 1907	Unknown			0.81			3.80	
58160	Apr. 15, 1908	----do----			7.10				
58403	May 7, 1908	----do----		4.63		7.97		2.19	^{c}1.42
63210	Jan. 6, 1909	----do----			4.25				
64141	Jan. 21, 1909	----do----			9.01	6.06			^{c}2.79
64275		Division of mines, sample No. F 31			0.86	19.58			0.27
64564	Feb. 8, 1909	Division of mines, sample No. F 32			1.53	17.02			1.34
65900	Feb. 17, 1909	Cave on Isabela Island (Not over 100 tons)			0.86	1.40			0.73
68316	Apr. 26, 1909	Kahoagan (Tabones) Island, north of Samar, near Lacang Bay			3.98	12.88			1.08
72620	Sept. 12, 1909	Dingle, Guimaras				18.20			
72620	----do----	----do----				23.12			
85887	Jan. 27, 1911	Guimaras ^{d}	19.51	2.08		4.84			1.29
87495	Apr. 12, 1911	Unknown	20.24	5.00		5.69	1.95	1.12	1.30
	1912	Batangas	0.00	5.69		8.85			
	1912	Marinduque ^{e}	15.38	3.52		7.06			0.92
	1912	Inlalapid cave near Norzagaray, Bulacan		1.31		6.73			

^{b} Natural water content.
^{c} Soluble in water.
^{d} Contains 6.60 per cent lime.
^{e} Contains 2.69 per cent lime.

It is only in unusually dry regions and in protected places that guano exists unleached. In many places, as seen by the above analyses, Philippine guanos have been deprived of their soluble ingredients, such as salts of ammonia and uric acid, which give them their chief value.

At the present time nearly all fertilizers are imported into the Philippine Islands from the United States and Europe. The cost of transportation and handling must be added to the original price. I see no reason why Philippine guanos should not be largely utilized, and as a basis of valuation I shall quote the following prevailing prices for fertilizers at California terminals from which shipment could be made to the Philippine Islands.[1]

Schedule of trade values, 1911–1912.[a]

Constituent.	Cents per pound.	Value in dollars per unit.
Nitrogen from blood	23.6	4.72
Nitrogen from tankage and bone	22.8	4.56
Nitrogen from ammonia sulfate	17.9	3.58
Nitrogen from nitrate of soda	14.1	2.82
Phosphoric acid from tankage	3.8	0.76
Phosphoric acid from bone (high in phosphoric acid, low in nitrogen)	5.0	1.00
Phosphoric acid from bone (low in phosphoric acid, high in nitrogen)	4.6	0.92
Phosphoric acid from bone and superphosphate	5.0	1.00
Available phosphoric acid from rock superphosphate	4.7	0.94
Phosphoric acid from Thomas Phosphate Powder	4.2	0.84
Potash from sulfate of potash	5.7	1.14
Potash from muriate of potash	4.9	0.98

[a] The base prices from which the above schedule is deduced are obtained as follows:
Blood and tankage, Chicago market quotations and freight to Pacific Coast terminals.
Bone meal, California manufacturers' estimates.
Sulfate of ammonia, New York quotations and a differrential freight rate based on Chicago production and delivery to California terminals.
Nitrate of soda, California manufacturers' estimates and actual sales.
Potash salts, New York quotations and differential freight rate (by sea) to California points.
Bone superphosphate, local manufacturers' estimates.
Thomas Phosphate Powder, local manufacturers' estimates.
Rock superphosphates, factory price, San Francisco Bay, and freight to Southern California points.

To these prices the freight rate from California terminals to the Philippines would have to be added in order to determine the

[1] Burd, John S., Commercial Fertilizers, *Bull. Univ. Cal. Agr. Exp. Sta.* (1911), **221,** 38.

value of commercial fertilizers with which Philippine guanos would have to compete.

It is impossible to estimate the value of the guano deposits for many of them are inaccessible and transportation is difficult. I believe that all of the guanos can be locally used to advantage, but those which are low in value would probably not bear transportation charges as an export.

112232——5

ROSELLE.

By D. S. PRATT.

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

Roselle, *Hibiscus sabdariffa* L., (Plate I) as a food product, stands in the unique position of being the sole representative of a type where the calyx supplies the chief edible portion of the plant. It has recently been introduced into the Philippine Islands by Mr. P. J. Wester, horticulturist of the Bureau of Agriculture, who describes the plant as follows:[1]

The roselle is malvaceous, and thus related to the okra, hollyhocks, and cotton, resembling the latter somewhat in habit. The leaves on the young plant are entire, changing as the plant grows larger to palmately five-parted, sometimes rather obscurely so. The leaves in the axils of which the flowers are borne are three-parted or entire. The flowers are large, pale yellow with a dark red eye, almost sessile, and usually borne singly in the leaf axils. In rich soils the plants sometimes exceed 2 meters in height with a like spread if the seed is sown early in the year and the plants are well cared for. Two very distinct types of roselle exist; one containing a red pigment that gives the brilliant color so characteristic of all products made from the plants of this type, and one lacking the pigment, all parts of the plant being greenish and the calyxes straw colored or whitish.

The plant is well known in most tropical or semitropical countries. It is grown chiefly for the calyx; however, the leaves are sometimes used as a substitute for spinach, and the fiber is of value in India. Although recently introduced into the Islands, the roselle is thriving and promises to add another source of profit to the agriculturist and at the same time a refreshing and acceptable adjunct to the tropical table. After flowering, the calyx thickens and enlarges until it assumes the appearance of a large bud. (Plate II.) In this condition they are harvested for use in making jam or jelly of a brilliant red color and pleasant acid taste, products very popular with those who have tried them.

[1] *Phil. Agr. Review* (1912), **3**, 125.

The similarity between roselle and cranberry, both in composition and use, makes a comparison between the two of decided interest from an analytical standpoint and is as follows:

TABLE I.—*Analyses of roselle and cranberry grown in the United States and roselle grown in the Philippine Islands.*

Constituents.	Roselle.[a]	Cranberry.[a]	Philippine roselle.
Water	88.91	88.53	82.49
Solids	11.09	11.47	17.51
Ash	0.89	0.25	1.26
Marc (insoluble matter)	6.67	4.60	7.39
Acid as malic	2.77	2.74	3.31
Reducing sugar as invert	0.83	1.90	0.82
Sucrose	0.03	0.10	0.24
Benzoic acid	absent	present	absent

[a] Analyses quoted from *Farm. Bull. U. S. Dept. Agr.* (1907), No. 307.

It is evident that although the roselle grown in the Islands contains less water and consequently more solid matter, still the actual food value is very low, and the product is to be considered more as a condiment than a food.

The most interesting point brought out by the analyses of Philippine roselle is the fact that the malic acid present consists entirely of the dextro rotatory modification. This form has heretofore been purely a laboratory product, and has never been isolated and identified in plant or fruit composition, although the lævo malic acid is a constituent of many fruits grown in temperate and tropical climates.

Malic acid was determined according to the accurate method of Dunbar and Bacon[2] as modified by the author[3] in which the greatly increased lævo rotation of a solution of the acid after treatment with uranyl acetate is utilized as a measure of the acid present. In the case of roselle, the change of rotation after this treatment was to the right while ordinary malic acid shows a change to the left. This could not have been due to tartaric acid, this acid being absent as shown by the potassium bitartrate [4] and basic magnesium tartrate tests.[5] To confirm the identity of the acid, it was precipitated with basic lead acetate, washed with

[2] *Cir. U. S. Dep. Agr. Bur. Chem.* (1911), No. 76.

[3] *Cir. U. S. Dep. Agr. Bur. Chem.* (1911), No. 87.

[4] *Bull. U. S. Dep. Agr. Bur. Chem.* (1910), No. 107, 86.

[5] Josef von Terentzy, *Analyst* (1908), 27, from *Chem. Ztg.* (1907), 31, 1119.

hot water, and liberated by hydrogen sulphide. After removing the lead sulphide, the solution on concentration deposited long feathery, deliquescent crystals. These were dissolved in water, and an aliquot portion titrated with standard alkali. Another portion was treated with uranyl acetate and polarized. The results of the titration and the polariscopic readings gave almost identical values for dextro malic acid. In this connection it is very interesting to note that the factor for computing the dextro acid is the same as that found for the ordinary or lævo modification, since the increased action of the uranyl compound on polarized light is of equal value for both acids but in opposite directions. To a third portion of the aqueous solution of the acid, an equal volume of alcohol was added and the calcium salt precipitated. This was filtered off and dried in a water oven at 100° to constant weight. A weighed amount was then fused with sodium carbonate and potassium nitrate mixture, dissolved in water, and the calcium precipitated as oxalate. On titration with standard potassium permanganate solution, the following results were obtained:

	Calculated for $C_4H_4O_5Ca.2H_2O$	Found (per cent).
Calcium	19.23	19.10

Another sample of the salt was dried to constant weight at 160°.

	Calculated for $C_4H_4O_5Ca.2H_2O$	Found (per cent).
Water of crystallization	17.31	17.30

Calcium was determined in the anhydrous salt.

	Calculated for $C_4H_4O_5Ca$	Found (per cent).
Calcium	23.25	23.32

Citric acid was shown to be absent by means of the delicate distillation method of the author.[6] Therefore, it is evident that roselle owes its pleasant acidity entirely to dextro malic acid. This is not confined to the calyx alone, but is distributed throughout the plant. The leaves contain about 1.25 per cent and the stems about 0.60 per cent, depending upon their age and location. The stems of the red variety also contain some coloring matter. It appears from these analyses that both stems and leaves contain sufficient flavoring material to render them suitable for use in connection with the calyxes except in those cases where it is desired to obtain a brilliantly colored jelly or jam. A comprehensive examination was made of roselle with reference to its

[6] *Cir. U. S. Dep. Agr. Bur. Chem.* (1911), No. 88.

adaptability as a source of flavoring sirup and of a beverage resembling wine. In both of these cases it is not essential to obtain a bright red product, and the great advantage of utilizing the entire plant made it worth while to experiment on this basis. The cost of the product is lower and the manufacture much more simple than in the other case where each calyx must be separately gathered. Needless to say a finer grade product, with better color and flavor, may be made from the calyxes alone. This is a matter of personal choice. As the procedure is similar in both cases, only that utilizing the entire plant need be given in detail.

ROSELLE SIRUP.

The flavoring sirup may be made according to the following directions, which may be modified to suit individual taste. The plant should be harvested while still of moderate growth, with tender stems, and at least half matured calyxes. While perfectly fresh, chop the entire plant into lengths of about 10 centimeters and pack in a keg or earthenware jar. Metal containers are attacked by the acid, and are not to be used at any stage of the process. Pour in sufficient boiling water to cover the plants, and then cover the keg to exclude dirt and molds as much as possible. Allow to stand two or three days to extract the soluble material, then filter through muslin or other suitable cloth. This gives a red liquid with a strong acid taste and pleasant fruity smell. Boil this liquid in an enameled dish until it reaches about one-third its original volume and add sucrose to suit the taste. Generally about equal volumes of sugar and concentrated juice will be satisfactory. Continue the boiling with constant stirring until the sugar is completely dissolved, and bottle while hot. If desired, the juice of a lime may be added to 1 liter of sirup. The resulting sirup has a very attractive taste and makes a refreshing product when added to water, or used as the basis for sherbets, water-ices, and soda water.

ROSELLE WINE.

Roselle wine may also be made from the entire plant, although here again a product with richer color and better flavor results from using only the calyxes. The plant is cut and treated as in making the sirup. After filtering through cloth, the juice is placed in a clean cask previously scalded out with boiling water. For every 4 liters of juice use 1 kilogram of sucrose made into a thick sirup with boiling water and poured into the juice. Suspend yeast in warm water, add this to the contents of the

keg, and mix thoroughly by stirring. The keg should now be carefully covered, or if one with the ends on has been used the bung may be stopped with loose cotton. To obtain a good wine, foreign ferments should be excluded. The cask is then put aside and allowed to remain undisturbed during fermentation. Within a week this will near completion. If a sparkling wine is desired, the juice is racked off before fermentation has stopped and stored in bottles with corks securely wired to prevent expulsion. If a still wine is to be made, the bottling is delayed until fermentation has ceased. Age will improve the flavor and bouquet, but the young wine is very attractive in taste and appearance. As made from the entire plant, it has a light reddish color and sweet refreshing taste. A complete analysis of the still wine so made gave the following result:

TABLE II.—*Analysis of roselle wine.*

	Per cent.
Total acidity as malic by titration	0.64
Total acidity as d-malic by polarization	0.62
Volatile acids as acetic	0.02
Alcohol by volume	8.80
Specific gravity	1.0631
Specific gravity dealcoholized wine	1.0762
Extract	19.79
Direct polarization°V	—37.20
Invert sugar	13.68
Sucrose	1.05
Protein $(N \times 6.25)$	0.092
Ash	0.380
P_2O_5	0.016

ILLUSTRATIONS.

PLATE I. ROSELLE IN THE FIELD (SINGALONG EXPERIMENT STATION, MANILA).

(From Philippine Agricultural Review.)
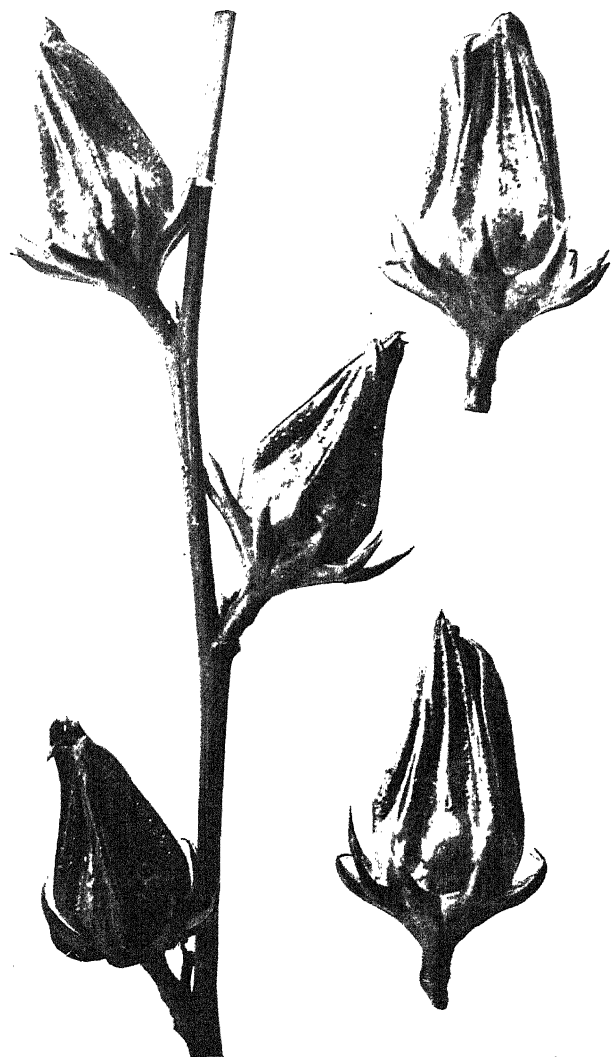
PLATE II.   "VICTOR" ROSELLE ABOUT FIVE-SIXTHS NATURAL SIZE.
(From F. B. 307, U. S. D. A., through the Bureau of Agriculture.)

REVIEWS.

The author advocates Gallic revolution rather than Germanic adaptation in methods of teaching physics. He believes that the present condition is deplorable in that high school teaching is arranged on college lines and deals largely with pure science, though nine-tenths of the pupils never reach college. The text-books of our fathers were written by practical, many-sided men, in nonmathematical language, for the instruction of the man on the street. Many editions were sold even to the nonstudent classes. But the present-day texts are more like cut-down college books. They bristle with formulas. Each subject is begun with a page of muddling definitions. In the laboratory the experiments are mostly overfine, wearisome measurements of constants or verifications of abstruse laws.

The author traces the origin of the trouble to the door of the colleges. Though their entrance requirements and inspections have brought order out of chaos, to them it is due that high school work is planned with reference to college entrance rather than to the needs of the pupils. The teachers, affected by the research fad, have pushed exact measurement, and have given the whole work a college-like content.

He believes that the remedy lies in bringing the classroom teaching into closer touch with the daily life of the boy. The texts should be purged of formulas. In illustrations and problems only things concrete to the student should be used. Definitions should not be given at the beginning of a treatment, but at the end after many simple illustrations have made the matter clear. Here is a specimen of a formula-free examination question which he suggests.

"Write after each word some fact which it suggests to you.

"work	time	wave	square
"positive	light	level	change
etc."			

It is doubtful whether most teachers are capable of devising

such tests, and whether the prospect of such a test would be an adequate incentive to a lazy student to do his daily work.

The author makes elaborate citations from Poincaré showing that energy is the unifying and simplifying idea in science, and from this argues that the elementary work should be built about this idea. The argument is almost too pretty in theory. He rightly emphasizes the importance of the reaction of the student, but the boy in whom the reformed teaching would produce the desired reaction is the boy who would probably go to college. He is in the minority for whom the course is not to be adapted. The problem is the *base* individual who is just on the point of throwing up the whole business. He needs the prospect of a clean-cut, searching examination. It is doubtful if the proposed scheme would help him.

The whole book is doctrinaire and to a great extent impracticable; it neglects the personal equation both of the teacher and student. Pedagogically, however, the book is extremely interesting and the discriminating reader will reap from it some new and useful ideas.

O. H. B.

The **Microscopical Examination of Foods and Drugs.** By Henry George Greenish, F. I. C., F. L. S. With 209 illustrations. 2d ed. Philadelphia. P. Blakiston's Son & Co., 1012 Walnut Street. 1910. Pp. i–xx + 1–386. Cloth. Price $3.

This book is a valuable reference for the food analyst, the pharmacist, and the student. The method of treatment is not changed from that followed in the first edition except that the chapter on fibers has been revised with the assistance of Miss Agnes Borrowman. Several additions have been made, and a chapter on the more commonly recurring adulterants of powdered foods and drugs has been added.

Characteristics of Existing Glaciers. By William Herbert Hobbs. Cloth. Pp. xxiv–301. Price $3.25 net. New York. The MacMillan Company. 1911.

This work is illustrated by six plates and 140 text figures.

The object of this book is to set forth views in relation to alimentation and depletion of glaciers, to emphasize the existence of two distinct types and one intermediate type of glaciers,

and to discuss the broader physiographic elements of the problem of glaciation.

Being in a locality lacking any evidence of former glaciation and one far south of the lowest limits to which glaciers have been traced, we are in no position to discuss this publication in relation to the Philippine Islands.

The book is interesting and follows a well thought out plan of discussion. It is comprehensively written and can be readily understood by one having but slight geological knowledge.

F. T. E.

THE BLACK SANDS OF PARACALE.

By PAUL R. FANNING and F. T. EDDINGFIELD.

(From the Division of Mines, Bureau of Science, Manila, P. I.)

In 1905 an investigation into the black sands of the Pacific slope was carried on by the United States Geological Survey.[1] The field covered by this investigation was so large that the economic possibilities presented by specific localities could not be discussed. After the publication of the article cited, various enterprises were started for treating black sands, but many failed, due to the lack of specific information in regard to the deposit worked.

The winning of gold from black sands presents a different problem for practically every district where they are found on account of the variation in the content of free and of combined gold; the physical condition of the grains of gold; the relative quantities of coarse and fine gold, magnetite, pyrite, copper, and platinum; and the character and treatment of the deposit. Therefore, in this investigation the black sands of one locality were taken, in order to determine their special characteristics. The locality selected was the Paracale mineral district in Ambos Camarines, Luzon, the one district where gold dredges were operating in the Philippine Islands at the time the experiments were begun. It was in this district that the first dredge was installed and this is the only one where dredging has been profitably carried on.

There are three areas in this district where paying placer deposits have been discovered: (1) Maliguit River, (2) Paracale

[1] Day, David T., and Richard, R. H., Bull. U. S. Geol. Sur. (1905), No. 285.

River, and (3) Gumaus River.   The Paracale River placer was
the first exploited, and it was this placer which was selected for
study.   The samples were obtained from the dredge of the
Paracale Bucket Dredging Proprietary Company Limited, and
represented cleanup concentrates from which the gold had sup-
posedly been removed.   The points discussed are: (1) The geol-
ogy of the deposit, (2) the physical and mineralogical character
of these concentrates, (3) the physical characteristics of the gold,
(4) the amount of free gold, (5) the amount of combined gold,
and (6) the best method for saving the gold values.

The method of determining these points was similar to any
complete ore-testing examination, namely: (1) Screen tests with
7 sizes; (2) magnetic separation of original and of each screen
into magnetic and relatively nonmagnetic; (3) assay value of
all products; (4) concentration tests; (5) amalgamation tests;
and (6) cyanide tests.

GEOLOGY.

The alluvium of the Paracale River for the most part lies in an
elliptical basin covering an area of several hundred hectares.
This is mainly in granite gneiss which is bounded practically on
all sides by diorite schist.[2]   The bed rock of soft, decomposed
granite gneiss is quite regular, having a uniform slope to the
east.   The alluvium varies in thickness from 5 meters at the
upper end to 14 meters near Paracale.

After the formation of the vein-ore deposits[3] and the establish-
ment of a drainage system, erosion continued until a condition
of comparative inactivity was reached.   This was followed by
a slight uplift, after which the gold, heavy minerals, and quartz
boulders from the veins were washed down and concentrated on
the bed rock.   At this period the erosion in general was only
moderate, as shown by the lack of large country-rock boulders
in the gravel deposits on the bed rock, and by the angular condi-
tion of the gold.   The presence of quartz boulders is explained
by their resistance to weathering in a country which must have
been rather extensively weathered before this period of moderate
erosion took place.

After the deposition of the gold-bearing gravels, a subsidence
occurred, and a bed of loam and clay and a thin bed of coral were
deposited.   Following this, a slight uplift in the western portion
of the formation occurred, which caused the deposition of a

[2] Fanning, P. R., *Min. Resources P. I. for 1910, Bur. Sci., Div. Min.* (1911),
21.
[3] *Ibid.*, 22.

second layer of gravel and sand. This was followed by another subsidence during which period another layer of clay and loam was deposited, and another coral growth was begun near the mouth of the river. At the present time an uplift is slowly taking place, as shown by the exposure of this coral. It would appear that the Paracale has been a tidal river since the deposit of the first gravels, with the exception of a possible period when the second sand and gravel bed was formed.

Numerous veins of quartz ore are found everywhere in the district, both in the gneiss and schist, but predominantly in the gneiss. These veins strike generally about north 10° east, and vary in width from a few centimeters to several meters. They have been worked by natives quite extensively as shown by the large number of pits, shafts, and open cuts in the surrounding hills. The natives worked only the surface oxidized ore, owing to its soft and free-milling character. The typical unaltered ore of the district is clear, white quartz, carrying a large percentage of pyrites and generally subordinate amounts of galena. The gold and the pyrites found in the alluvium were principally derived from the erosion of these veins. The magnetite and ilmenite came partly from the veins, but mostly from the country rock.

The alluvium is made up of layers of clay, clayey sand, and gravel. An occasional layer of tough blue clay near the gravel causes trouble in dredging by carrying away metallic gold which it picks up as it passes over the tables. Many of the quartz fragments in the gravels contain visible gold. Some have been found with pockets of crystallized gold out of which from 20 to 30 grams of gold were taken. Contrary to what would be expected, the coarser fragments are found near the mouth of the Paracale River. Many well-rounded, water-worn boulders were found which weighed almost a ton. These decrease in size toward the west, and are very small in the upper portion of the deposit. This is probably due to the fact that the boulders have come from the quartz veins of the side hills. Two sections of this alluvium have been described in the Mineral Resources of the Philippine Islands. The first, described as near Paracale,[4] has in vertical section:

From 4 to 5 meters of barren clay and loam.
A few centimeters of coral in places.
Gray clay, irregular in thickness, carrying values.
Sand, gravel, and quartz fragments; irregular in thickness, rich in gold.
The bed rock is soft decomposed schist.

[4] Ferguson, H. G., *Min. Resources P. I. for 1908, Bur. Sci., Div. Min.* (1909), 22.

The second is described as follows:[5]

From 0 to 1.5 meters, soil, nipa, etc.
From 1.5 to 7.6 meters, sand and gravel with some values.
From 7.6 to 11.5 meters, heavy black loam, with considerable decayed vegetable matter.
From 11.5 to 12.2 meters, gravel, pay streak.
The bed rock is white, soft, decomposed granite-gneiss.

The first section must have been near the mouth of the Paracale River below the contact of the gneiss and schist.

DREDGE CONCENTRATES.

The concentrates saved on the tables of the dredge are estimated to be as follows:

TABLE I.—*Composition of concentrates.*

Mineral.	Weight (per cent.)
Magnetite	51
Ilmenite	16
Pyrite	21
Nonmetallic	12

In examining the tables prepared by Day and Richards under magnetic separation of black sand in California, it is noted that ilmenite is found in comparatively few examples. The black sands of Paracale contain a large percentage of ilmenite. These grains almost invariably are well rounded and waterworn, but show practically no alteration or decomposition in a thin section. The ilmenite grains are among the largest caught on a 10-mesh[6] sieve, and are more abundant than the magnetite grains. This relation changes with the smaller sizes, and the magnetite content increases until it becomes more than 50 per cent of the material. The magnetite is more angular than the ilmenite, and, while usually fresh, shows signs of oxidation and alteration.

A screen test was made on a sample of about 2 kilograms of black sand, showing that on a 10-mesh sieve the material was approximately 25 per cent iron pyrites, 20 per cent magnetite and ilmenite, 2 per cent cemented black sand and quartz, and 5 per cent nonmetallic. The material caught on the 20-mesh consisted approximately of 90 per cent magnetite and ilmenite, 6 per cent iron pyrites, and 4 per cent nonmetallic. The percentage of iron pyrites increases slightly in the smaller sizes, but definite estimates could not be made.

[5] Smith, W. D., *Min. Resources P. I. for 1909, Bur. Sci., Div. Min.* (1910), 11.
[6] The sizes of the various sieves used are given on page 223.

An important characteristic of this sand is the large amount of iron pyrites caught on the 10-mesh screen and the comparatively small amount caught on the 20-mesh screen. Tests made in connection with this investigation have shown that in all probability the values in the black sands other than free gold are largely due to the richness of these pyrites.

The nonmetals are unimportant. Of these zircon is probably the most abundant. It is found in characteristic crystals of 1 millimeter or less in length. The small amount shown in the screen test is no indication of the amount of this heavier nonmetal actually present in the original sands. The character of the rock formation of the district is such that large amounts of garnet, zircon, pyroxene, and biotite should result from its weathering, and should concentrate with the black sand. Insignificant amounts of metallic iron, galena, and metallic lead are found in the table concentrates. The iron and metallic lead are undoubtedly, for the most part, foreign materials derived from the dredge or dredge operation. Copper coins, rings, and various metallic articles manufactured by man have also been found.

Several distinct classes of gold are found. One class is very light yellow, well crystallized, and is usually found attached to quartz grains (Plate I). Some pieces are so light in color as to appear nearly white, probably due to a large silver content. The second class is also crystalline and associated with quartz, but is of a much darker color, apparently being stained with iron oxide. The third class is generally yellow, but shows decidedly worn and rounded surfaces as if it had traveled a greater distance than the majority of the gold. The fine gold is crystalline and angular, showing that it had moved but a short distance from its source. A large number of perfect octohedrons was noticeable. These were very small and would for the most part pass an 80-mesh screen. These crystals were often joined, forming trees of wire gold.

DREDGE OPERATION.

At present the placer deposit is worked by a 3.5-foot loose-connected, or link-bucket, type of dredge which has been able to handle about 10,000 cubic meters of material per month, although designed to handle from 20,000 to 25,000 cubic meters. The buckets at present dump into a revolving screen or trummel, which serves merely to break up the clay and to screen out the boulders and pebbles greater than 1 inch in diameter. The screen product passes over a series of tables fitted with cross riffles underlain with coco matting. These riffles quickly become

filled with black sand concentrates, forming a compact, smooth surface over which the sands flow, carrying away an enormous percentage of concentrates and causing the loss of a large amount of fine gold. Mercury is not used in the riffles. Some of the tables near the screen are cleaned up once a day; others are cleaned once a week, and the tables farthest from the screen are cleaned only about once a month. These concentrates are collected in a box and are screened through a punched metal plate with round openings about 6 millimeters in diameter. The material passing through the screen flows over a well of mercury to catch the amalgamable gold, and from there to a few riffles where unamalgamated gold, pieces of amalgam, and mercury are caught. This operation recovers the major portion of the free gold, a large percentage of the coarse gold bound up with quartz, only a very small percentage of the very fine gold, and practically none of the fine gold bound up in quartz and pyrites. The cleanup concentrates, after receiving this treatment, generally are saved for future treatment.

SAMPLING AND ASSAYING.

Lot No. 1.—This represents the black sand concentrates from which the gold had been collected in the regular cleanup by hand-panning without the use of mercury. The gold was supposed to have been completely panned out, but its abundance as revealed in our tests showed that hand-panning is very inefficient.

The lot, which weighed about 100 kilograms, was cut into 4 sections of 25 kilograms each. Section I was cut into halves and one of the halves was pulverized through 60-mesh and then cut into 4 parts. Each part was divided into 2 splits crushed on a bucking board through 150-mesh. The splits representing the 4 parts gave the following average assays per ton: 235.24 pesos,[1] 210.26 pesos, 217.26 pesos, and 203.80 pesos. Section II was similarly treated, except that the half pulverized through 60-mesh was cut into 2 splits which were independently cut down and put through 150-mesh. The samples representing the 2 splits gave average assays of 299.48 pesos and 306.74 pesos, respectively. Comparing the two sections, we find an average of 216.88 pesos for section I and an average of 303.10 pesos for section II.

As these checks were very unsatisfactory, a sample of the original was bucked through 150-mesh; the assays of this varied

[1] One peso Philippine currency equals 50 cents United States currency.

from 190.06 pesos to 200.40 pesos. The results of the sampling are more clearly shown in a table as follows:

TABLE II.—*Results of sampling. Lot. No. 1.*

Product.	No.	Assay per ton.	Differences.
		Pesos.	*Pesos.*
Sections cut from original..............................	1	303.10	86.22
	2	216.88	
Sections cut from original at 60-mesh................	1	235.24	
	2	211.26	31.44
	3	217.26	
	4	203.80	
Section cut from original at 150-mesh...............	1	190.06	10.34
	2	200.40	

As shown by Table II, the 2 sections cut from the original show a difference of 86.22 pesos in value; sections cut after the ore has been put through 60-mesh show variations of 31.44 pesos, and sections cut after the ore has been put through 150-mesh show variations of 10.34 pesos. Fine grinding gives much closer checks, but the fact that considerable variations occur even in the 150-mesh product shows the exceedingly irregular distribution of the values (due to the metallics) and the practical impossibility of obtaining absolute checks on lot 1 under ordinary conditions of sampling.

Lot No. 2.—This represents the black sand concentrates from which the gold had been collected by passing it over the well of mercury and riffles as described on page 218. The gold content was considerably less than in lot 1, showing the advantage of using mercury in the cleanup; yet abundant free gold was present, indicating that even this method is inadequate.

A quarter of lot 2 was cut out and pulverized through 60-mesh. This was divided into 4 parts, and each part was sampled and assayed separately. The following results were obtained: 110.80 pesos, 109.56 pesos, 114.20 pesos, 114.40 pesos. These results are far more concordant than those obtained on lot 1, as is to be expected, since these are the amalgamation tails from the dredge cleanup from which a great deal of the free gold had been removed. Notwithstanding the use of mercury in the cleanup, some free gold still remained and was visible on the screens and was recovered in our amalgamation tests.

Lot No. 3.—This represents a sample of the dredge tailings

which had been concentrated by hand-panning. The sample assayed 16.40 pesos per ton, and gives not only an indication of the value of the black sands distributed generally through the ground, but also an idea of the loss of gold by the dredge.

The lot assayed 16 pesos per ton, and checks were readily obtained. This was due to its low value and to the small amount of free gold present.

Influence of free gold upon the sampling.—Free gold was repeatedly picked out of the coarse meshes of the screen tests on lot 1, and the amalgamation tests showed a considerable percentage of free gold. The amount of free gold in the various splits is variable, and causes variations in the assays of those splits. The variations of visible gold in 3 splits of lot 1 are shown in the following table:

TABLE III.—*Visible gold in splits. Lot No. 1.*

Split No.	Screen.	Weight of gold in 100 grams of sample.
		Milligrams.
1	On 10	29.6
2	do	18.5
3	do	12.9
1	On 20	14.2
2	do	23.9
3	do	11.7

It is seen that in 3 splits of the original, the gold picked from the 10-mesh varies from 12.9 to 29.6 milligrams, and for the 20-mesh varies from 11.7 to 14.2 milligrams. Computing from these data, the variations in the visible gold cause a difference of 29.90 pesos per ton in the value of the sample.

In bucking down the samples for assay, pellets frequently were obtained on the screen (150-mesh), and the varying amounts indicated irregular distribution of free gold in the various splits. To illustrate, after pulverizing a sample so that it would pass 60-mesh, rolling thoroughly, and then cutting twice for assay samples, it was found that one of the splits retained screen pellets equivalent to 1 peso per ton and the other retained pellets equivalent to 13.22 pesos per ton of the original material. The complete assay was 299.48 pesos per ton for the former and 316.74 pesos for the latter, a difference due to irregular distribution of the free gold as indicated by the pellets on the screen.

In assaying the screen products after division into magnetic and nonmagnetic products, the greatest differences in duplicate assays occurred in the products containing the most free gold. This was true notwithstanding the fact that the majority of the free gold had previously been eliminated by amalgamation. These assay differences are shown in Table IV in which the pulp was bucked through 150-mesh and then assayed in triplicate. The maximum differences are given.

TABLE IV.—*Showing assay variations in screened products. Lot No. 1.*

| Screen. | Maximum assay differences in triplicate assays. | | Gold amalgamated for one ton of original. |
	Magnetic product.	Nonmagnetic product.	
Mesh.	*Pesos.*	*Pesos.*	*Pesos.*
10	15.60	10.94	23.96
20	5.96	10.60	39.22
40	none	10.60	12.16
60	none	none	7.74
80	none	1.24	4.34
100	none	1.24	3.04
150	none	none	1.20
(—)150	none	none	3.68

As shown by Table IV, the triplicate assays check almost perfectly in the finer screen products, but check very poorly in the 10- and 20-mesh. Evidently this is due to the greater abundance of free gold in the coarser meshes (see column 4) which makes the assay sampling exceedingly difficult even when the pulp is pulverized through 150-mesh. The table also shows that the magnetic products check in their respective assays very much closer, as a rule, than do the nonmagnetic products. This distinction is due, likewise, to the free unamalgamable gold remaining in the nonmagnetic portion. The theory that the free gold is the cause of variations in duplicate pulp assays is also borne out by the fact that in the majority of cases little difficulty was encountered in obtaining close checks on products after amalgamation; whereas, before amalgamation, in assaying the heads, great differences occurred and frequently required from 6 to 8 assays in order to obtain a dependable average.

ASSAYING OF THE CONCENTRATES.

Occasionally some free gold was caught where the sample was put through 60-mesh preparatory to the final splitting. As a rule, however, the gold was so brittle as to be reduced in size along with the remainder of the sample. When the final sample

was bucked through 150-mesh, a considerable number of gold pellets frequently were caught on the screen. These pellets were scorified or cupelled direct and the weight of gold was calculated into the sample. For example, in making the assay of the 10-mesh product of the screen test on lot 1, 0.04220 gram of gold was picked out by hand, and 0.0220 gram was caught on the 150-mesh screen. The picked gold calculated into the sample made a difference of 154.62 pesos, and the pellets made a difference of 166.60 pesos. The pulp assay was only 269.56 pesos, making a total assay value of 590.78 pesos. On the 20-mesh product the picked gold made a difference of 141.20 pesos, while the pellets made a difference of only 1.90 pesos. With the finer meshes no pellets were obtained upon bucking down the sample sufficiently to pass a 150-mesh screen.

To find the best method of assaying the pulp, experiments were carried on as shown by Table V.

TABLE V.—*Showing effect of different charges in assaying. Lot No. 1.*

(Original pulp through 150-mesh; 15 grams used in each charge.)

Charge.[a]	Assay.	Average.	Variation.	Pour.
Grams.	*Pesos.*	*Pesos.*	*Pesos.*	
30 litharge, 70 soda _____	183.04 194.20	188.62	11.16	Clean.
60 litharge, 40 soda _____	180.34 194.20	188.26	7.86	Some lead shot in the slag.
90 litharge, 30 soda _____	155.54 158.24	156.88	2.60	Much lead shot in the slag.
30 litharge, 60 soda, nails ____	190.06 200.40 192.74 195.44	194.66	10.34	Clean.

[a] In all charges 2.5 grams of borax glass and 10 grams of powdered silica were added; a borax cover was used. When nails were not used, 3.1 grams of argols were added.

In order to obtain a clean pour, it was found necessary to use a long fusion at a high temperature. The time of fusion varied from one to one and one-half hours, and the muffle had to be kept at a yellow to white heat during the last half or three-quarters of the time. From the above table it is evident that the high soda was better than high litharge charge, yet the best results were obtained with the ordinary nails charge. It is to be noted that a variation of 10.34 pesos was obtained even with

the nails charge. In order to secure close checks, 150-mesh is none too fine and 200-mesh would probably have given better results.

Another series of experiments was run on some amalgamation tails, and the results obtained are shown in Table VI.

TABLE VI.—*Assay experiments upon amalgamation tails.*

(Pulp through 150-mesh; 15 grams used in each charge.)

Charge.[a]	Assay.	Average.	Variation.	Pour.
Grams.	*Pesos.*	*Pesos.*	*Pesos.*	
30 litharge, 60 soda	4.96 4.96	4.96	none	Clean.
90 litharge, 30 soda	1.86 3.72	2.88	1.86	Much lead shot in the slag.
30 litharge, 60 soda, nails	6.58 6.58	6.58	none	Clean.

[a] In all charges 2.5 grams of borax glass and 10 grams of silica were added ; a borax cover was used. When nails were not used, 3.1 grams of argols were added. A long fusion at high temperatures was used in each case.

The first charge (low litharge, high soda) gave a clean pour, but low result. The second charge (high litharge, low soda) gave a very shotty pour and a low result. The nails charge gave a clean pour and the highest result. It is evident that when the free gold has been removed by amalgamation, there is no difficulty in doing perfect work, provided the conditions stated are properly fulfilled.

SCREEN TESTS.

The screens used for the tests were purchased from Braun-Knecht-Heimann & Co. for regular laboratory use. They are of the usual copper, woven-wire type, and new screens only were used. The screen openings were measured under the microscope, and the averages of both directions are shown in Table VII.

TABLE VII.—*Measurements of screen openings.*

Screen.	Average screen opening in mm.
10	2.00
20	1.00
40	0.40
60	0.25
80	0.187
100	0.166
150	0.09

The distribution of weights and values are shown in Tables VIII and IX.

TABLE VIII.—*First screen test.   Lot No. 1.*

Screen.	Weight.	Weight.	Assay per ton.	Gold distributed in one ton of original.	
Mesh.	*Grams.*	*Per cent.*	*Pesos.*	*Per cent.* [a]	*Pesos.*
10	309.9	10.09	446.40	30.10	44.80
20	447.7	14.52	366.50	35.80	53.20
40	394.9	12.94	161.30	14.00	20.80
60	317.5	10.34	95.30	6.60	9.80
80	437.2	14.28	62.80	5.93	8.90
100	407.3	13.32	37.60	3.45	5.20
150	451.9	14.71	14.50	1.40	2.10
(—)150	301.6	9.80	41.30	2.72	4.10
Total	3,065.0	100.00	---------	100.00	148.90

[a] Based on gold accounted for rather than heads assays, owing to the great variation in such assays.

TABLE IX.—*Second screen test.   Lot No. 1.*

Screen.	Weight.	Weight.	Assay, per ton.	Gold distributed in one ton of original.	
Mesh.	*Grams.*	*Per cent.*	*Pesos.*	*Per cent.*	*Pesos.*
10	327	9.62	590.80	43.00	56.40
20	450	13.16	244.10	24.40	32.10
40	432	12.64	108.40	10.05	13.20
60	377	11.02	69.80	5.87	7.70
80	455	13.32	69.80	7.08	9.30
100	459	13.47	41.40	4.03	5.30
150	512	15.02	17.00	1.90	2.50
(—)150	405	11.82	40.10	3.67	4.80
Total	3,417	100.00	---------	100.00	131.30

The two screen tests were made on widely separated splits and show very similar features, although varying in the actual assays of the various products. As can be seen from these two tables the weights on each screen are fairly equal, but the coarse meshes are by far the richer. In the first screen test the 10-mesh product assayed 446.40 pesos per ton, and the other mesh products decreased in value down to 150-mesh. The 150-mesh product assayed only 14.46 pesos per ton and marks the approximate position where the values begin to ascend. An interesting feature of these tests is that the gold distributed in the 10- and 20-mesh products is more than double the gold in all the other meshes combined. The values are plotted in text figures 1, 2, and 3. Fig. 1 shows the curve for the assays per
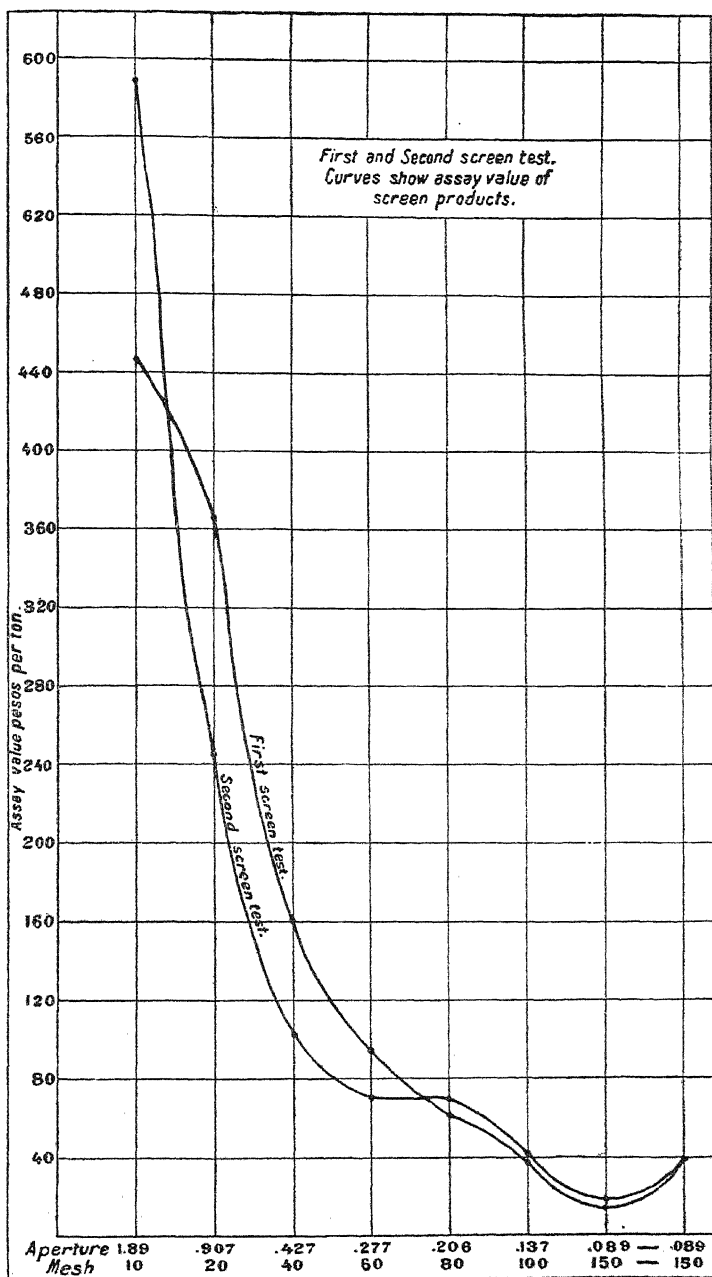
Fig. 1.

ton, fig. 2 shows the accumulative percentages of gold, and fig. 3 shows the curve for the gold distributed in 1 ton of original.

The high assays of the coarse meshes are largely due to the coarse free gold present. This is shown by Table X, which gives the values of the assay pulps and of the pellets saved (picked from the screen plus pellets saved on the 150-mesh screen in bucking down for assay) and calculated in proportion to the weight of the sample.

TABLE X.—*Showing assay of pulps and pellets of screen products. Lot No. 1.*

	First screen test.			Second screen test.		
Screen.	Assay of pulp.	Pellets.	Total.	Assay of pulp.	Pellets.	Total.
Mesh.	*Pesos.*	*Pesos.*	*Pesos.*	*Pesos.*	*Pesos.*	*Pesos.*
10	88.40	358.00	446.40	269.60	321.20	590.80
20	194.10	172.40	366.50	100.80	143.30	244.10
40	158.30	3.00	161.30	101.30	2.00	103.30
60	92.70	2.60	95.30	69.80	none	69.80
80	62.90	none	62.90	69.80	none	69.80
100	37.60	none	37.60	41.30	none	41.30
150	14.50	none	14.50	16.90	none	16.90
(—)150	41.30	none	41.30	40.10	none	40.10

It can be seen (1) that the pellets form the major portion of the value on the 10-mesh, (2) that they form about an equal value on the 20-mesh, (3) that they almost disappear on the 40- and 60-mesh, and (4) that no pellets were obtained on the finer screens nor found when pulverizing these finer products through 150-mesh preparatory to assaying.

CONCENTRATION TESTS.

In the treatment of black sands, concentration is generally given the place of first importance, and the majority of published data is a consideration of this phase of the treatment. However, it is to be remembered that such treatment generally is applied to black sands as they are found in the ground, or else to those which have been only slightly concentrated. The samples treated by us had previously been concentrated and so were distinctly different from the black sands generally under consideration.

Panning tests.—Panning tests were made upon the sample of lot 1 to determine: (1) If the free gold could be separated, (2) if a high-grade shipping product could be obtained, (3) the loss

First and Second screen test.
Curves show accumulative
percentages, weights and gold.

Gold curve, average.

Weight curve average.

| Aperture | 1.89 | .907 | .427 | .277 | .206 | .137 | .089 — .089 |
| Mesh | 10 | 20 | 40 | 60 | 80 | 100 | 150 — 150 |

Fig. 2.

First and Second screen test.
Curves show values distributed
in one ton of original.

First screen test.

Second screen test.

| Aperture | 1.89 | .907 | .427 | .277 | .206 | .137 | .089 — .089 |
| Mesh | 10 | 20 | 40 | 60 | 80 | 100 | 150 — 150 |

Fig. 3.

of gold in the tails and slimes, and (4) the probable action of a Wilfley table.

The results of the tests are given in Table XI.

TABLE XI.—*First panning test. Lot No. 1.*

Product.	Weight.		Assay value per ton of product.	Value distrib- uted in 1 ton of original.	Composition of product.			
					Gold in original.	Pyrite.	Iron minerals.	Metallic minerals.
	Grams.	*Per cent.*	*Pesos.*	*Pesos.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Original heads..	100	....	210.30	210.30	....	....	....	....
Gold recovered .	....	....	....	63.40	30.00	....	....	....
Middlings: Nonmag- netic......	34.40	34.40	128.40	42.90	20.28	50	40	10
Magnetic...	52.41	52.41	2.40	1.30	0.59	3	97	....
Tailings	10.76	10.76	16.80	1.80	0.86	20	10	70
Slimes	2.43	2.43	....	101.90	48.2	....	....	....

In the test tabulated above, the sample was panned by hand, giving (1) free gold, (2) middlings, (3) tailings, and (4) slimes. The gold was cupelled and weighed; the middlings were treated by magnet to give magnetic and nonmagnetic products; the tailings were assayed directly; but insufficient slimes were obtained to make a satisfactory assay, although the gold content was very high. This test was merely preliminary, but it showed the presence of high values in free gold.

Where 1 ton of black sand was concentrated by panning, 63.40 pesos of gold were obtained giving an extraction of 30 per cent. This left a middlings product worth 51.20 pesos per ton, and a tailings product worth 16.80 pesos per ton. If the middlings were treated magnetically, we could obtain a nonmagnetic product worth 128.40 pesos per ton and a magnetic product worth 2.40 pesos per ton. The great advantage of magnetic treatment was at once indicated by this test and led to a magnetic test as shown on page 230 where the original was magnetically treated and gave a nonmagnetic product containing 97.21 per cent of the gold.

The results of the panning test given in Table XI were confirmed by a second test in which the sample was crushed through 40-mesh and extreme care taken in the panning. In this test only gold and tailings were separated. The tailings were then given magnetic treatment. The results are tabulated as follows:

TABLE XII.—*Second panning test. Lot No. 1.*

(Ore crushed through 40-mesh.)

Product.	Weight.		Assay value per ton of product.	Value distrib- uted in 1 ton of original.	Gold in original.
	Grams.	Per cent.	Pesos.	Pesos.	Per cent.
Original heads	200		210.30	210.30	
Gold recovered				91.80	43.50
Tailings:					
Nonmagnetic	91.4	45.7	102.80	51.00	24.3
Magnetic	107.5	53.7	13.20	7.10	2.9
Loss in slimes	1.1	0.55	61.40	61.40	29.3

As seen from this table, from 1 ton of concentrates, 91.80 pesos or 43.5 per cent of the gold was saved as free gold by means of panning. The tailings had a value of 51.40 pesos per ton. If these tails were treated magnetically, we could obtain a nonmagnetic product worth 102.80 pesos per ton and a magnetic product worth 13.20 pesos per ton. If we consider the gold and the nonmagnetic product, we find a total saving of only 67.8 per cent of the gold by a method involving (1) crushing through 40-mesh, (2) concentration on a Wilfley-type table, followed by (3) magnetic treatment of the tailings. Such a saving is too small for practical consideration.

A salient feature of these preliminary tests was the fact that a large percentage of the gold is so fine as to be lost in the slimes even under the most careful conditions of panning.

Similarly, dredging must lose a large amount of this type of gold. In addition, dredging loses practically all of the gold bound up in the black sand and quartz. The black sands saved in the cleanups are negligible in comparison with the amount present in the ground, and the quartz boulders picked out of the chutes represent only a small fraction of the quartz present. It would seem apparent that dredging is losing more than 50 per cent of the total gold, free and combined, in the ground. These figures have been confirmed by sampling the dredge tailings, concentrating and assaying them, estimating the total amount of this class of sand wasted, and comparing the result with the output of the dredge. This does not mean that the dredge lost 50 per cent of the value of the ground as estimated by drive-pipe tests. The drive-pipe tests themselves merely show the free gold and hence probably show less than 50 per cent of the gold actually in the ground.

MAGNETIC SEPARATION.

The magnetic treatment of the middlings, as performed in the panning tests, just described, showed the marked association of the gold with the nonmagnetic material. It seemed apparent that if the original product were treated magnetically we could obtain a nonmagnetic product containing a large percentage of the gold. Accordingly a sample of lot 2 was magnetically treated and gave the following results:

TABLE XIII.—*Magnetic separation test. Lot No. 2.*[a]

Product.	Weight.	Weight.	Assay per ton.	Gold distribution in 1 ton of original.	
	Grams.	*Per cent.*	*Pesos.*	*Pesos.*	*Per cent.*
Original _____	3,595	_____	102. 70	102. 70	_____
Nonmagnetic_____	2,100	58.3	170. 40	99. 50	97.21
Magnetic _____	1,495	41.7	7. 50	3. 20	2. 79

[a] Ratio of nonmagnetic to magnetic=1.7 to 1.

The separations were made by means of a small electro-magnet moved by hand over the ore spread in a thin layer on a sheet of paper. This method does not actually represent the work of machines such as the Wetherhill and Ding, but it gives an approximate idea of the weights and values of the products. The magnet has a core 20 centimeters long with a diameter of 2.5 centimeters, and is wound with about 1,000 turns of No. 19 copper wire, B. and S. gauge. A current of 1.5 amperes and 107.5 volts was used in all tests. After picking up the magnetic material, the magnet was moved to a second sheet of paper where the product was dropped, spread out, and the magnetic minerals again picked up. The necessity of this second treatment lies in the tendency of the gold to be picked up with the magnetite in the first treatment. When sized products were used, this tendency practically disappeared, although with moist samples it still would be a serious consideration.

If 100 tons of concentrates worth 102.70 pesos per ton were treated magnetically, we could obtain 58.3 tons of nonmagnetic product worth 170.40 pesos per ton and representing an extraction of 97.21 per cent.

In order to study the association of the gold with the nonmagnetic material, a sample of lot 1 was screened through a series of meshes, and each screen product was separately amalgamated and then magnetically treated. This clearly shows (1) amalgamable free gold on each mesh, (2) gold associated with the nonmagnetic portion, and (3) gold associated with the magnetic portion. The results are given in Table XIV.

TABLE XIV.—*Screen, amalgamation, and magnetic treatment test. Lot No. 1.*

Screen.	Weight.	Gold picked.	Gold amalgamated.	Total free gold saved.	Assay of nonmagnetic.	Assay of nonmagnetic, including free gold.	Assay of magnetic.	Weight of non-magnetic.	Weight of magnetic.
Mesh.	Grams.	Mgms.	Mgms.	Mgms.	Pesos per ton.	Pesos per ton.	Pesos per ton.	Grams.	Grams.
10	487.0	90.50	7.50	98.00	96.30	410.50	41.50	373.5	113.5
20	657.5	157.00	4.90	161.90	264.60	1,773.60	12.00	129.5	528.0
40	643.0	....	50.80	50.80	207.50	660.10	4.00	135.5	507.5
60	546.5	....	32.50	32.50	43.80	197.20	3.20	256.5	290.0
80	734.5	....	20.10	20.10	72.30	138.46	3.20	367.5	367.0
100	569.0	....	12.85	12.85	13.40	65.70	3.20	295.0	274.0
150	880.5	....	5.20	5.20	21.50	34.70	4.50	466.5	414.0
(—)150	560.9	....	15.50	15.50	11.20	73.20	3.70	300.4	260.5

Column 3 shows the gold picked by hand from the 10- and 20-mesh; this was added to the total gold saved as given in column 5. The large amount of free gold saved on each mesh is strikingly shown. This gold was added to the assay of the non-magnetic (of column 6) in order to obtain the total gold, either free or combined, in the nonmagnetic as shown in column 7.

It is clearly seen that on every mesh the nonmagnetic product assays many times greater than the magnetic. The ratio of these assays with, and without, free gold is shown in Table XV.

TABLE XV.—*Showing ratios of assays of the nonmagnetic to the magnetic portion.*

Screen.	Ratio of assay of nonmagnetic to magnetic.	Ratio of total assay of nonmagnetic, plus free gold, to magnetic.
10	2.3 to 1	9.9 to 1
20	22.0 to 1	148.0 to 1
40	52.0 to 1	165.0 to 1
60	13.7 to 1	61.5 to 1
80	22.7 to 1	43.4 to 1
100	4.2 to 1	22.8 to 1
150	4.3 to 1	7.0 to 1
(—)150	3.5 to 1	22.8 to 1

These ratios show the association of the gold with the non-magnetic on every mesh. As can be seen (column 3), on 40-mesh the maximum ratio of 165 to 1 and on the 150-mesh the minimum ratio of 7 to 1 are obtained.

Screen Amalgamation and magnetic test.
Curves show the accumulative percentages
of weight.

| Aperture | 1.89 | .907 | .427 | .277 | .206 | .137 | .089 — .089 |
| Mesh | 10 | 20 | 40 | 60 | 80 | 100 | 150 — 150 |
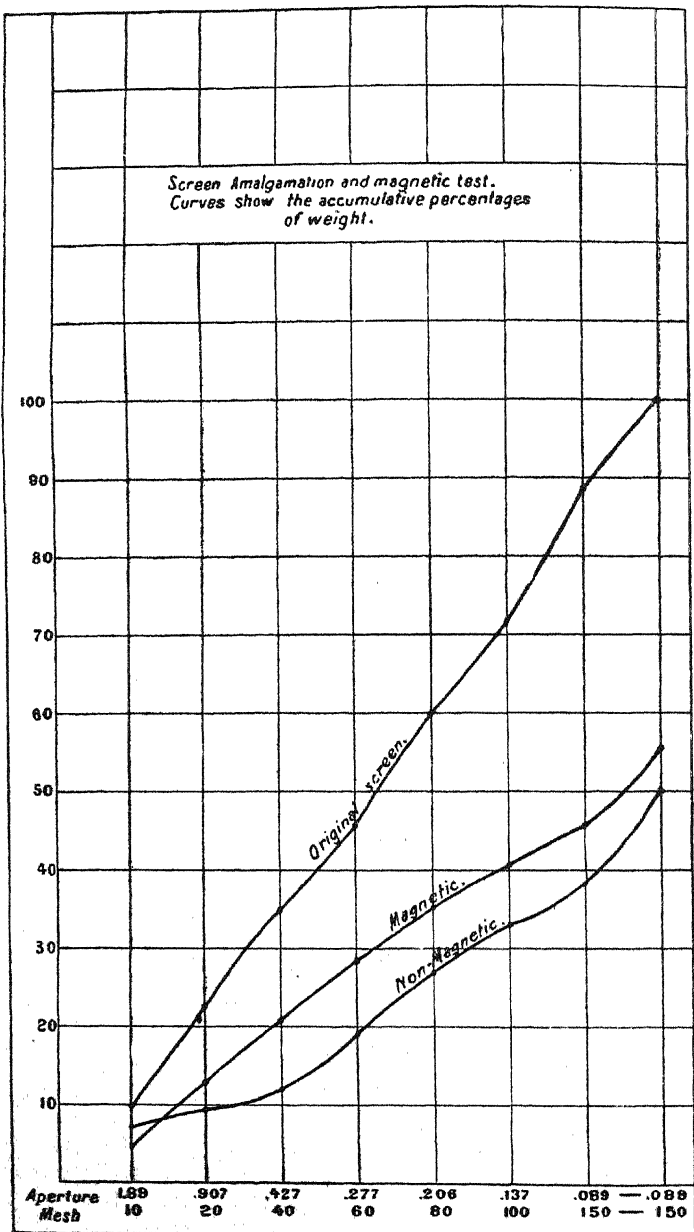
Fig. 4.

A new table was calculated to show the actual recovery on each screen, and the distribution of values in the magnetic and non-magnetic portions after amalgamation *where a ton of original is treated.* This is shown in Table XVI.

TABLE XVI.—*Screen amalgamation test to accompany Tables XIV and XVII.*

| Screen. | Gold amalgamated. | Gold in amalgamation tails. [a] | | Total in amalgamation tails. |
		Nonmagnetic.	Magnetic.	
Mesh.	*Pesos.*	*Pesos.*	*Pesos.*	*Pesos.*
10	22.96	7.22	0.82	8.04
20	39.22	6.70	1.24	7.94
40	12.16	5.34	0.60	5.94
60	7.74	2.22	0.18	2.38
80	4.34	5.24	0.24	5.48
100	3.04	0.78	0.16	0.94
150	1.20	2.00	0.40	2.40
(—)150	3.68	0.66	0.08	0.74
Total	94.34	30.16	3.80	33.96

[a] Based on gold accounted for and evidently low.

As shown in this table, a ton of original worth 128.30 pesos is screened to give 8 products, and on the 10-mesh 22.96 pesos were saved by amalgamation; on the 20-mesh, 39.22 pesos were saved; etc. The tailings of each screen were then divided into nonmagnetic and magnetic portions, and the 10-mesh nonmagnetic contained 7.22 pesos worth of gold, the 20-mesh nonmagnetic contained 6.70 pesos, etc. By the totals it is seen that out of the 128.30 pesos contained in the original, 94.34 pesos are saved by amalgamation, 30.16 pesos are found in the nonmagnetic after amalgamation, and 3.80 pesos are found in the magnetic. It is to be noted that the heads assay of 128.30 pesos is assumed from the totals of the accountable gold and in comparison with other assays of lot 1; this value is low and it seems that there has been a considerable loss of gold in the process as explained on page 239.

By calculation it was found that 96.5 per cent of the gold is found in the nonmagnetic as indicated by the results given in Table XIV. The percentage for each mesh is shown in Table XVII.
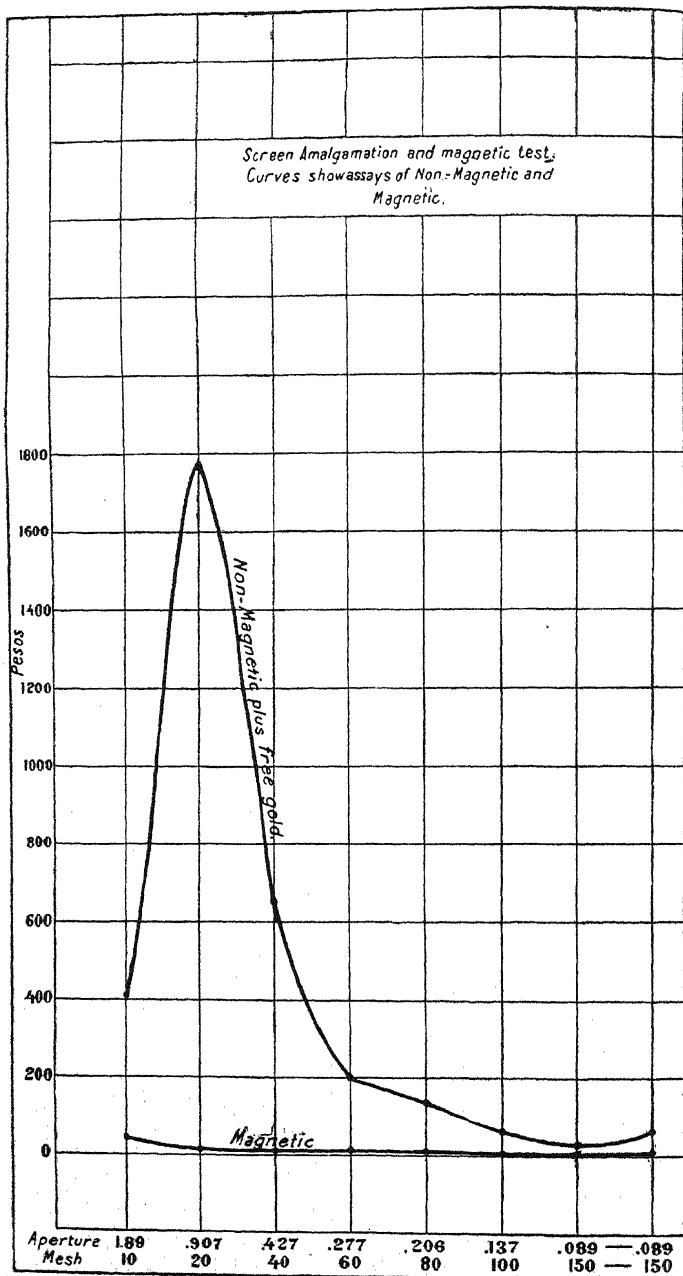
Fig. 5.

TABLE XVII.—*Percentages of total gold in nonmagnetic and magnetic portions.*

Screen.	Gold in nonmagnetic.	Gold in magnetic.
Mesh.	*Per cent.*	*Per cent.*
10	23.00	0.70
20	35.30	0.97
40	13.80	0.31
60	7.80	0.14
80	7.80	0.18
100	2.97	0.14
150	3.37	0.13
(—)150	3.37	0.13
Total	96.51	2.94

This table shows that 23 per cent of the gold in the original is found with the 10-mesh nonmagnetic, 35.3 per cent is found with the 20-mesh nonmagnetic, etc. The decrease in percentage with the finer meshes is clearly shown.

The association of only 2.94 per cent of the gold with the magnetic would indicate the efficiency of magnetic separation to eliminate a 'large bulk of low-grade tailings and leave a small bulk of high-grade concentrates for shipment. Where the cost of shipping is a factor, as in the Paracale district, the importance of these results can hardly be overestimated, as they indicate the possibility of concentrating the values into a small high-grade product and thus making a great saving in the cost of shipping and smelting.

In order to determine the effect of magnetic separation upon the *dredge tailings,* a large sample was taken, panned by hand, and concentrates obtained. These concentrates (lot 3) assayed 16.40 pesos per ton, and a portion was separated into nonmagnetic and magnetic products. The nonmagnetic product, weighing 880 grams, assayed 24 pesos per ton; and the magnetic product, weighing 630 grams, assayed 5.82 pesos per ton. This test again proved the marked association of the gold with the nonmagnetic material.

A Wilfley-type table treating the dredge tailings would probably give concentrates equal to the value of lot 3, or 16.40 pesos. Such a product could not be magnetically treated with the object of shipping the nonmagnetic product, for such a product, as indicated, would have a value of only 24 pesos. This is insufficient to pay shipping and smelting charges. Should a large bulk of 16-peso product be obtained by concentration tables

Screen Amalgamation and magnetic test.
Curves show distribution of values in one
ton of original.
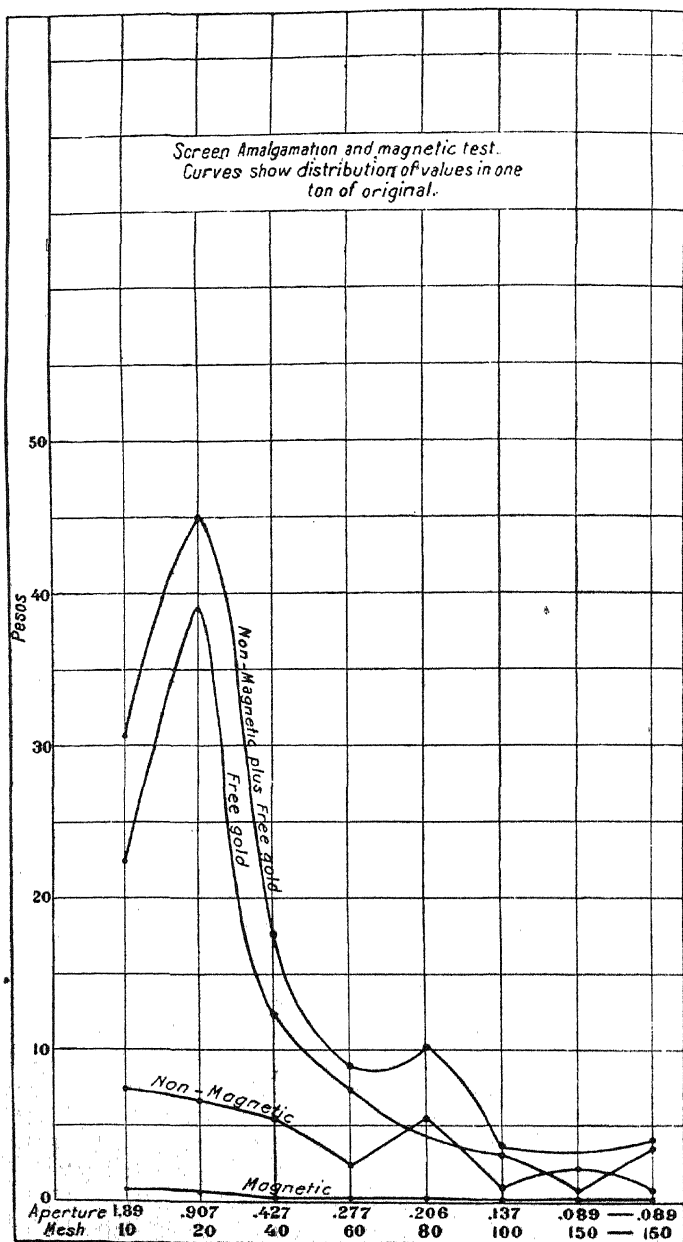
Fig. 6.

it could very effectively be treated by means of cyanidation as will be discussed later.

SHIPMENT OF CONCENTRATES.

The magnetic separation tests showed that a high-grade shipping product could easily be separated. This means a saving of weight and a corresponding saving in cost of shipping and smelting.

Analysis of the nonmagnetic product showed the following:

TABLE XVIII.—*Analysis of nonmagnetic shipping products. Lot No. 2.*

Constituent.	Per cent.
Insoluble in Hcl	35.36
SiO_2	13.26
Al_2O_3	9.43
Fe_2O_3	53.93
CaO	0.96
TiO_2	9.60
S	12.32
Gold	[a] 170.40
Silver	trace

[a] Pesos.

The cost of magnetic treatment, including drying, should not be over 3 pesos per ton. The total cost of shipping would amount to about 16 pesos, and the smelters would make a charge of about 12 pesos per ton of dry weight. The Tacoma Smelter has stated in a letter:

In a general way we pay for 95 per cent of the value of the gold and silver contents, figuring the gold at $20 per ounce and silver at New York quotations date of arrival of the ore at the smelter. No pay for gold unless the assay is 0.05 ounce per ton or more and no pay for silver unless the assay is one ounce per ton or more. Smelting charges from $6 to $7 per ton of 2,000 pounds dry weight. Where large shipments are made these figures would probably be bettered.

The total cost can be given approximately as follows:

TABLE XIX.—*Cost of magnetic treatment, shipping, and smelting.*

Factor.	Pesos.
Magnetic treatment (1.7 to give 1 ton)	5.00
Sacking and loading on steamers	4.00
Lighterage, Manila,	3.00
Wharfage, Manila,	1.00
Storage	1.00
Freight to Tacoma	6.00
Insurance, sampling, etc.	5.00
Smelting charges	12.00
Deductions	10.00
Approximate total per ton	47.00

The magnetic test of lot 2 gave a nonmagnetic product worth 170 pesos per dry ton, and this could be shipped at a total cost of about 47 pesos, leaving a profit of about 123 pesos per ton of shipped product. On the other hand, direct shipment of the concentrates *without* magnetic treatment would cost about 42 pesos per ton and with a product worth about 103 pesos per dry ton; this would give a profit of about 61 pesos per ton of shipped product. However, for true comparison of the methods, the relative tonnages and the extractions should be taken into consideration as follows:

TABLE XX.—*Comparison of shipment costs.*

Factor.	Magnetic separation and shipment.	Direct shipment.
Value of product	1.7 tons of original, worth a total of 175 pesos, separates to 1 ton worth 170 pesos.	1.7 tons at 103 pesos equals 175 pesos.
Cost of treatment	5 pesos for 1.7 tons	None.
Loss in tailings	5.25 pesos	None.
Shipment and smelting cost	47 pesos	71 pesos for 1.7 tons.
Total cost	57.25 pesos	71 pesos.
Profit on 1.7 tons of original	112.75 pesos	104 pesos.

As shown by this table, if 1.7 tons of original are treated magnetically and shipped, there is a profit of about 113 pesos, while if these 1.7 tons were shipped direct, the profit would amount to 104 pesos. This indicates an advantage in favor of magnetic treatment previous to shipment. Before deciding this point, it would be advisable to make more extensive tests using a well-known type of machine.

AMALGAMATION TESTS.

In making amalgamation tests the sample was placed in a 1-liter bottle; about 2 parts by weight of water, 6 to 8 cubic centimeters of mercury, and about 1 gram of sodium hydroxide were added, and the bottle revolved for one hour. The mercury and the gold amalgam were then collected by panning and the mercury was dissolved with nitric acid. The gold, which generally was beautifully crystallized, was then cupelled with the

addition of silver and lead, the silver-gold bead parted, and the gold weighed after the usual annealing.

In some of the tests the mercury after amalgamation was badly floured, and considerable difficulty was met in collecting the amalgam by panning. This was generally overcome by the addition of a little nitric acid which cleaned the floured mercury and permitted the minute specks to run together into larger globules which were easily panned out. The addition of fresh mercury was also tried and found very beneficial in collecting the mercury and amalgam.

Various kinds of apparatus were tried to see if the mercury would settle to the bottom of a cone and there be drawn off, but when the mercury was floured these proved of little advantage. When emptying the bottle, it was customary to invert, revolve rapidly, and then let the mercury drop out into a pan, whereas the pulp was emptied into a separate pan. It was always necessary to collect the mercury in this separate pan as some was always floured.

The percentage of gold saved in many cases is based on the actual recovery and not on the assay of the tailings. It will be noted that in some cases there is gold unaccounted for by the gold saved and assay of the tailings. This is in part due to the variations in the samples, but it is also due to an actual loss of gold in the process. Some of this loss can be traced to the retention of gold by the bucking board, but where excessive it probably occurred in the wash water. In making amalgamation tests, there was a marked tendency of the gold and floured mercury to float off the pan and be lost in the water. At first the precaution of carefully settling the slimes was not taken, and the losses in some of the tests are thus accounted for. This is important as it indicates that in practise great care must be exercised in panning the borings of the placer test-holes. It shows that a large percentage of the fine gold in those borings will not be caught by the ordinary methods of panning. In order to prevent this loss, it was found necessary to agitate the water and tailings very thoroughly, to allow it to settle for twenty-four hours, and to decant and boil the residue to dryness.

In order to find the amalgamable gold on each screen, the test described under magnetic separation (Tables XIV to XVII) was made, and by rearrangement the following is shown:

TABLE XXI.—*Screen, amalgamation test. Lot No. 1.*

Screen.	Weight.	Weight.	Assay of product before amalgamation, per ton.	Assay of tails per ton.	Weight of gold saved.	Gold saved in each product.
Mesh.	*Grams.*	*Per cent.*	*Pesos.*	*Pesos.*	*Mgrams.*	*Per cent.*
10	487.0	9.63	324.70	83.30	98.00	74.2
20	657.5	12.95	375.00	61.60	161.90	83.5
40	643.0	12.67	141.20	46.20	50.80	65.3
60	546.5	10.72	93.70	22.20	32.50	76.3
80	734.5	14.42	70.50	36.40	20.10	48.4
100	569.0	11.19	36.20	8.40	12.85	76.8
150	880.5	17.31	·20.50	13.50	5.20	34.1
(−)150	560.9	11.11	40.60	7.50	15.50	81.5
Total	5,078.9	100.00			396.85	

Each mesh was separately amalgamated, and the pieces of gold picked out of the 10- and 20-mesh were credited to amalgamation. On the 10-mesh, 90.5 milligrams of gold were picked, while 7.5 milligrams were recovered by amalgamation; on the 20-mesh, 157 milligrams were picked, while 4.90 milligrams were recovered by amalgamation. On the other meshes no gold was picked and the gold was saved entirely by amalgamation.

This table shows that the 10-mesh product assayed 324.70 pesos per ton before amalgamation, and assayed 83.30 pesos per ton after amalgamation. This indicates that 74.2 per cent of the gold on this mesh can be saved by amalgamation. The figures for the other meshes are given and the following points can be seen: (1) The weights on each screen are fairly equal; (2) the assay values decrease from the 10-mesh downward and this decrease applies (although less regularly) to the tailings as well; (3) considering each screen alone, the percentage of recoverable gold shows no system of increase or decrease in comparison with the individual recoveries on other screens; thus, on the 10-mesh the recovery is 74.2 per cent, on the 80-mesh it is 76.8 per cent, etc. However, when the amount of gold amalgamated per ton of original is shown for each screen, it is evident that the greatest amount of gold is recovered in the coarse meshes and decreases progressively with the finer screens. This is shown in Table XXII.

TABLE XXII.—*Screen, amalgamation test. Lot No. 1.*

(Showing distribution in a ton of the original sand.)

Screen.	Gold in heads.[a]	Gold amalga-mated.	Gold in tailings.	Reco-very.
Mesh.	*Pesos.*	*Pesos.*	*Pesos.*	*Per cent.*
10	31.00	22.96	8.04	17.82
20	47.16	39.22	7.94	30.40
40	18.10	12.16	5.94	9.47
60	10.12	7.74	2.38	6.05
80	9.82	4.34	5.48	3.38
100	3.98	3.04	0.94	2.37
150	3.60	1.20	2.40	0.93
(—)150	4.42	3.68	0.74	2.87
Total	128.30	94.34	33.96	73.29

[a] The loss in this operation largely was due to sliming and repeated grinding. The original assay of the heads gave a value of 211 pesos.

The effect of grinding the original ore through various meshes, followed by amalgamation, is shown in Table XXIII.

TABLE XXIII.—*Amalgamation tests. Lot No. 1.*

Product.	No.	Assay of heads per ton.	Assay of tails per ton.	Gold saved per ton.	Gold saved.	Discrep-ancy.
		Pesos.	*Pesos.*	*Pesos.*	*Per cent.*	*Pesos.*
Original	1	211.20	76.80	84.00	39.7	(—)50.40
Original put through 60-mesh	2	235.20	91.80	115.70	49.4	(—)27.70
	3	202.80	67.40	110.00	54.5	(—)25.40
	4	216.00	93.00	124.70	57.6	(+) 1.70
	5	211.20	67.40	156.00	73.8	(+)12.20
Original through 80-mesh	6	235.20	49.60	177.40	76.6	(—) 8.20
Original, tube-milled for 6 hours	7	169.80	15.20	154.60	91.0	none

The original ore gave an extraction of 39.7 per cent actual gold recovered, the 60-mesh gave an average of 58.8 per cent, the 80-mesh gave an extraction of 76.6 per cent, and the tube-milled product gave an extraction of 91 per cent. These results show a steady increase of extraction with greater pulverization as would naturally be expected. Variations occur in the extractions of the 60-mesh ore, and it is evident that there is either a variation in the amount of free gold in the different splits, or else there is an actual loss of gold in some of the tests.

In order to see if the irregularities in the extraction percentages of duplicate tests were due to varying fineness in the samples, screen tests were made on numbers 3, 5, 6, and 7 of lot 1, Table XXIII, and the results are given in Table XXIV.

TABLE XXIV.—*Screen tests. Lot No. 1.*

Test No.	Product.	20-mesh.	40-mesh.	60-mesh.	80-mesh.	100-mesh.	150-mesh.	(—)150-mesh.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
3	Original through 60-				14.10	19.30	22.10	44.40
5	mesh.				15.05	20.37	22.85	41.80
6	Original through 80-mesh					17.26	25.60	57.20
7	Original, tube-milled for 6 hours		2	3	11.00	14.00	11.00	54.00

This table shows not only the fineness of the 60-mesh, 80-mesh, and tube-mill products, but it shows, as in 3 and 5, that the opposite splits of the 60-mesh product are practically identical. Hence the greater extraction by amalgamation (Table XXIII) in test 5 over that of 3 was due to variations in the free gold present and to losses of gold in the process of panning.

At one time the Paracale dredge sent its quartz and table concentrates (after cleaning out the free gold) to a small Huntington mill for subsequent treatment. The work of this mill was stated to be very unsatisfactory and the bullion recovered was small in consideration of the value of the ore treated. A great deal of the quartz is so hard as to require stamps, although for the treatment of the concentrates a Huntington mill would be better. It is very likely that if this mill had treated concentrates only, it would have done far more efficient work.

The results given in Table XXIII indicate the work which can be expected of a Huntington mill treating concentrates only. A mill using a 40-mesh screen should give results similar to tests 2, 3, 4, and 5 of this table, while a mill using a 60-mesh screen should give results similar to test 6. Judging from this, a Huntington mill would give an extraction of from 40 to 70 per cent depending on the screens, condition of the plates, etc.

In testing ground in order to find out the values, the borings are placed in buckets and are later panned by hand, frequently using mercury to collect the gold. This method does not collect

all the gold, although it is probably equivalent to the actual recovery to be expected of the dredge. When we amalgamated the original sample we were able to save only 39.7 per cent of the total gold present, or about 76 per cent of the free gold. There was an actual loss of 24.3 per cent in gold which floated off and was not caught by the mercury nor saved with the tailings. When testing the ground, under the methods of rough treatment practised, it is unquestionable that there is a loss of gold due to such floatation.

The amalgamation tests on lot 2 are given as follows:

TABLE XXV.—*Amalgamation tests. Lot No. 2.*

Product.	No.	Weight of sample.	Assay of heads.	Gold saved, weight.	Gold saved per ton of ore.	Gold saved.	Assay of tailings.	Discrepancies.
		Grams.	Pesos.	Mgrms.	Pesos.	Per cent.	Pesos.	Pesos.
Original through 60-mesh.	1	900	114.20	40.58	54.10	47.5	59.50	(—)0.60
	2	950	109.60	26.60	32.60	30.0	67.30	(—)8.70
Original through 100-mesh.	3	680	110.80	29.40	51.70	46.6	64.40	(+)0.29
	4	110	114.20	31.15	52.90	46.4	58.10	(—)3.11

The screen test of the ore through 60- and 100-mesh shows the following:

TABLE XXVI.—*Screen tests. Lot No. 2.*

Product.	60-mesh.	80-mesh.	100-mesh.	150-mesh.	(—)150-mesh.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Through 60-mesh	none	13.6	21	20.3	45.1
Through 100-mesh	none	none	none	10.28	89.72

As seen from Table XXV, the amalgamation tests at 60-mesh show an average of 38.7 per cent recoverable, while at 100-mesh an average of 46.5 per cent was obtained. It is evident that finer grinding releases more gold and increases the extraction. However, it is clear that the increase is only nominal and not as great as might be expected from the difference in fineness. As shown by the screen tests tabulated in Table XXVI, the 100-mesh product contained 89.72 per cent through (—)150-mesh, while the 60-mesh product contained only 45.1 per cent through (—)150-mesh. This indicates that on this lot, fine grinding is not a very efficient method of liberating the gold. Furthermore, the maximum recovery of only 46.5 per cent is altogether too

small for practical consideration. A Huntington mill will probably do no better on such a concentrate, and in all probability its work will be nearer the result indicated by numbers 1 and 2 rather than 3 and 4.

The tests indicate that the treatment of the concentrates by amalgamation is unsatisfactory unless the product is tube-milled. When this is done a fair extraction may be expected.

CYANIDATION TESTS.

The attention of metallurgists has been directed within recent years to the cyanidation of *mill* concentrates, and several plants are now in operation, such as the Goldfield Consolidated and Alaska-Treadwell mills, where the success of this phase of cyanide treatment has been fully demonstrated. It has generally been found that the essential features of such treatment are fine grinding, agitation, and considerable time, although there is a wide range of variation depending upon the nature of the ore.

We have investigated the possibility of cyaniding the concentrates from the dredge, and it is possible that these tests are the first which have been published on this treatment applied to such a product. In consideration of the number of dredges which are saving black sands in their cleanups, it would be well if this method of treatment were given a thorough investigation in other parts of the world. The results obtained were so highly successful as to lead to the belief that many dredges, now throwing away large quantities of low grade concentrates, could cyanide these with considerable profit.

Cyanidation tests on lot No. 1.—A preliminary cyanide test was made on an original sample of lot 1, and it was found that 25 per cent of the gold could be recovered in twenty-four hours using agitation with 0.26 per cent potassium cyanide (KCN) solution and a ratio of solution to ore of 1:1. The consumption of cyanide was 450 grams (1 pound) per ton of ore. This test indicated that ordinary leaching is of little benefit, a fact confirmed by the coarseness of the free gold and the impenetrability of the mineral crystals.

A sample of lot 1 was then tube-milled for six hours, and the screen test showed 98 per cent passing 150-mesh. The product was then divided into 2 sections, one for amalgamation and subsequent cyanide treatment, the other for direct cyanide treatment. As shown by the following tables, the total extraction is exceedingly high where amalgamation is used previous to

cyanidation and a high extraction can be obtained without amalgamation when sufficient time is given to dissolve the gold.

TABLE XXVII.—*Cyanidation tests. Lot No. 1.*[a]

(Ore was tube-milled; 98 per cent passed 150-mesh.)

Test No.	Weight	Assay of heads per ton.	Assay of tails after amalgamation, per ton.	Extraction by amalgamation.	Assay of tails after cyanidation.	Extraction by cyanidation alone.	Total extraction.	Strength of KCN solution.	Ratio of solution to ore.	Consumption of KCN per ton of ore.	Time.
	Grams.	Pesos.	Pesos.	Per ct.	Pesos.	Per ct.	Per ct.	Per ct.		Pounds.	Hours.
1	120	299.50	120.70	59.8	3.80	96.8	98.8	0.29	3 : 1	1.0	48
2	120	299.50	120.70	59.8	3.00	97.4	99.1	0.29	3 : 1	2.0	96
3	120	299.50	(b)		60.40	79.9	79.9	0.23	3 : 1	3.0	24
4	120	299.50	(b)		6.20	98.0	98.0	0.23	3 : 1	10.4	96

[a] In these tests, the ore was agitated in a bottle and about 2 kilograms (4 pounds) of lime per ton of ore were added.

[b] Cyanided direct.

As shown by tests 1 and 2 of Table XXVII, the highest extraction is obtained by cyanidation when preceded by amalgamation. Where this is done, a total extraction of 98.8 per cent is obtained in forty-eight hours. By doubling the time of agitation, the extraction is increased only 0.3 per cent. The low cyanide consumption is particularly to be noted, and it is evident that the ore contains few or no minerals injurious to cyanide solutions.

As shown by tests 3 and 4 of the same table, an extraction of 98 per cent can be obtained without previous amalgamation, the essential requirement being time, for in twenty-four hours the extraction was only 79.9 per cent, whereas in ninety-six hours the extraction increased to 98 per cent. It is to be noted that the consumption of cyanide is larger in tests 3 and 4 where amalgamation was not used, and this to some extent is due to the greater amount of gold actually dissolved.

The presence of a large amount of coarse gold in lot 1 has been repeatedly mentioned and it would naturally be expected that cyanidation would be very ineffective on such gold. It is undoubtedly necessary either to remove this gold by amalgamation or to break it up by fine grinding. The gold evidently is in such form as to be broken up by ordinary tube-milling, for, upon screening the tube-milled product through 100-mesh, no pellets were found and only a few flakes were revealed on the 150-mesh screen. This brittle feature of the gold applies to

this particular lot, and can not be expected necessarily to apply to other lots, and the design of a plant to treat such ore by cyanidation should undoubtedly be arranged to permit amalgamation after tube-milling. Such a system would greatly decrease the time necessary for the high extraction and lead to a much lower consumption of cyanide. However, this would be counterbalanced somewhat by the extra cost and difficulties of amalgamation.

Cyanidation tests on lot No. 2.—A series of tests were then made upon lot 2 in order to confirm the results obtained in cyaniding samples of lot 1. In this new series of tests a sample was crushed through 60-mesh, amalgamated, and the tailings cyanided. Another sample was crushed through 100-mesh, amalgamated, and the tailings cyanided. Still another sample was tube-milled for six hours and cyanided direct.

TABLE XXVIII.—*Cyanidation tests. Lot No. 2.*[a]

Test No.	Product.	Weight.	Assay of heads, per ton.	Assay after amalgamation, per ton.	Extracted by amalgamation.	Assay of tails after cyanidation, per ton.	Extraction by cyanidation alone.	Total extraction.	Strength of KCN solution.	Ratio of solution to ore.	Consumption of KCN, per ton of ore.	Time.
		Gms.	*Pesos.*	*Pesos.*	*P. ct.*	*Pesos.*	*P. ct.*	*P. ct.*	*P. ct.*			*Pounds*	*Hours.*
[b]1	Ore through 60-mesh	160	109.60	67.40	38.5	28.90	57.0	73.4	0.29	3 : 1	7.8	48
[b]2	Do	160	109.60	67.40	38.5	12.00	82.3	89.0	0.29	3 : 1	8.0	96
3	Ore through 100-mesh	270	110.80	64.50	41.6	5.00	92.3	95.4	0.29	3 : 1	5.4	48
4	Do	270	110.80	64.50	41.6	4.00	93.7	96.5	0.29	3 : 1	4.8	96

[a] In cyanidation the samples were agitated in a bottle using about 2 kilograms (5 pounds) of lime per ton of ore.

[b] Extraction based on tailings assays.

As shown by the tests of Table XXVIII, when the ore is put through 60-mesh, amalgamated, and cyanided, there is obtained an extraction of 73.4 per cent in forty-eight hours and 89 per cent in ninety-six hours. When the ore is put through 100-mesh, amalgamated, and cyanided, there is obtained an extraction of 95.4 per cent in forty-eight hours and an extraction of 96.5 per cent in ninety-six hours. It is evident that additional fine grinding gives a much higher extraction in the same time.

To obtain the comparison with cyanidation direct, not preceded by amalgamation, the tests shown in Table XXIX were made.

TABLE XXIX.—*Direct cyanidation test. Lot No. 2.*

(Ore tube-milled. Heads assay 110 pesos per ton.)

Test No.	Assay of tails. [a]	Time.	Ex-traction.	Con-sumption KCN per ton of ore.
	Pesos.	Hours.	Per cent.	Pounds.
1	95.10	1	13.6	0.06
2	95.10	2	13.6	0.06
3	89.00	5	19.1	0.10
4	78.50	8.5	28.6	0.40
5	65.20	24	40.8	2.40
6	57.40	30	47.6	2.30
7	23.20	50	78.8	6.8
8	29.60	74	74.7	4.2
9	23.20	96	78.8	4.8
10	23.20	98	78.8	4.8

[a] Calculated from solution assays.

The screen test of the product is given as follows:

TABLE XXX.—*Screen test. Lot No. 2 after tube-milling.*

Product.	Weight.	Weight.
Mesh.	Grams.	Per cent.
On 60	0.5	0.39
On 80	0.8	0.62
On 100	2.5	1.95
On 150	6.0	4.68
(—)150	118.0	92.38
Total	127.8	100.00

In these tests the ore was tube-milled for six hours, and as shown by the screen analysis of Table XXX, 92.38 per cent passes 150-mesh. A sample weighing 1,470 grams was agitated in a small Pachuca tank using compressed air. At the beginning, the solution had a strength of 0.24 per cent KCN, and after ninety-eight hours the strength was 0.16 per cent KCN. The pulp had a thickness of 3 parts of solution to 1 part of dry ore, and about 5 pounds of lime per ton of ore were added. Samples were taken by dipping, and the results of the tailings assays were checked by solution assay. It was noticed in taking these samples that the heavier minerals tended to concentrate near the bottom of the apparatus and so could not be caught in the sample. This produced not only imperfect sampling, but inefficient agitation as well. The assays of the tailings unmistakably revealed improper sampling, as after one hour the tailings

assays indicated about 80 per cent extraction, whereas the solution assay showed an extraction of only 13.6 per cent. Therefore, the solution assay was used, and the assays of the tailings were discarded in all samples; except the last, where it was possible to filter the whole of the tailings and sample accurately after the usual washing and drying. In these last samples the tailings checked closely with the solution assays.

As shown by Table XXIX, there is an extraction of 13.6 per cent in one hour, and this increases with time until in ninety-eight hours there is an extraction of 78.8 per cent with a cyanide consumption of 2.17 kilograms (4.8 pounds) per ton of ore. It is to be noted that after fifty hours the extraction shows no increase whatever, even though the time was continued up to ninety-eight hours. It is probable that the inefficient agitation had much to do with the relatively low extraction, and that further tests (not possible with us owing to lack of samples) with proper agitation would give an extraction equal to that obtained in similar tests on lot 1.

TABLE XXXI.—*Summary of cyanide tests.*

Product.	Mesh.		Extraction by amalgamation.	Extraction by cyanidation.		Total extraction.
			Per cent.	*Per ct.*	*Hours.*	*Per ct.*
	Original _____		Not amalgamated _____	25.0	24	25.0
Lot No. 1. Assays about 300 pesos per ton for the sample taken.	98 per cent through 150-mesh.	1	59.8	96.8	48	98.8
		2	59.8	97.4	96	99.1
		3	Not amalgamated __	79.9	24	79.9
		4	Not amalgamated __	98.0	96	98.0
Lot No. 2. Assays about 110 pesos per ton.	Original through 60-mesh.	1	38.5	57.0	48	73.4
		2	38.5	82.3	96	89.0
	Original through 100-mesh.	1	41.6	92.3	48	95.4
		2	41.6	93.7	96	96.5
	92 per cent through 150-mesh.	1	Not amalgamated __	13.6	1	13.6
		2	Not amalgamated __	40.8	24	40.8
		3	Not amalgamated __	78.8	98	78.8

As summarized in the above table, lot 1, uncrushed, will give a very small extraction, but after tube-milling a high extraction is obtained in forty-eight hours where previous amalgamation is used. A high extraction can be obtained without previous amalgamation only when the time is greatly increased. lot 2 will give a much higher extraction at 100-mesh than at 60-mesh where both products have been previously amalgamated. The tube-milled product without previous amalgamation gave only a moderate extraction even with long time. This moderate extraction could probably be increased by more efficient agitation. The general conclusion is that cyanidation will give a high extraction when the following process is used: (1) Tube-milling, (2) amalgamation, (3) air agitation, (4) filter pressing or decantation, and (5) zinc precipitation. Insufficient samples were on hand to make confirmatory tests on a large scale, and exact determination of the best strength of solution, thickness, etc., was not possible.

Many mills which formerly shipped their concentrates to smelters are now using cyanidation for the recovery of the values. A few notes on this practise which is very similar in the essentials to the required practise on the black sand concentrates are herein given. The agitation of the pulp may be done in either a suitably designed Pachuca or in a tank using mechanical stirrers. Hamilton[8] recently advocated the latter type. As stated by him:

For agitation, an ordinary tank with mechanical stirrer and a small air-lift at the periphery for aerating, will usually be found much more convenient than a Pachuca, especially when the plan is to settle and decant. Not the least trouble is experienced concerning the sticking of the paddles if they are set sufficiently high above the bottom for the granular part of the charge to settle beneath them, the only other precaution necessary being to give a sufficient speed to the paddles so that they will pick up the charge again from the bottom. If these two points are observed devices for raising and lowering the paddles are quite unnecessary.

It is generally known that decantation has drawbacks among which the incomplete washing out of the dissolved values is a serious consideration. The trend of recent practise is toward filter-pressing which permits nearly perfect washing combined with the use of small amounts of solutions. As stated by McFarren:[9]

At first the rich cyanide solution was removed by decantation as none of the filtering devices were suitable. However the Kelley filter press was found adaptable and is now being used for filtering concentrates.

[8] *Eng. & Min. Journ.* (1912), **93**, 841.
[9] *Salt Lake Review,* April 30 (1912), 19.

With the nonpressure leaf filters nearly an hour is consumed in getting a cake upon the leaves during which time the sulphides by their high specific gravity, settle out of the pulp making it practically impossible to get a good cake. The Kelley, being a pressure filter, makes a cake within a few minutes and before the sulphides can settle. While there are other types of pressure filters, none of them seem able to give the careful wash necessary when working with the rich solutions associated with sulphides cyanidation.

Hamilton[10] advocates the use of a horizontal vacuum filter as follows:

The most suitable filter would appear to be a horizontal vacuum filter, with sides 6 in. high, and arranged so that it might be tilted almost to the vertical for dumping the washed residue. A square or oblong table filter of this kind about 8×12 ft. would treat 500 lb. of concentrate at each charge, the pulp, solution, and water would be filtered to a finish in each case, and then the table would be tilted, the ledge on the lower side removed, and compressed air allowed to enter under the cake which would slide off towards the dump.

At the Alaska-Treadwell mill, the concentrates, worth about 120 pesos per ton gold value, are tube-milled and given a preliminary agitation with a 2-pound lime solution. The pulp is then thickened by decantation and cyanided. It is then filtered in Kelley presses, and the solution passes to Merrill precipitation presses. The precipitate is treated with acid and then melted in an oil-burning furnace, and refined in a Faber du Faur tilting furnace. It has been found that one 5- by 11-foot tube-mill can grind 88 tons of concentrates per twenty-four hours. The feed contains 38.5 per cent moisture and shows on 100-mesh, 48.7 per cent; on 200-mesh, 41.5 per cent; and through 200-mesh, 9.8 per cent. The discharge shows on 100-mesh, 10.1 per cent; on 200-mesh, 26.4 per cent; and through 200-mesh, 63.5 per cent. The tube-mills use 59-horsepower, and turn at a speed of 27 revolutions per minute.

As stated in the Mineral Industry:[11]

G. E. Welcott describes the treatment of concentrates at the North Star and Central mills at Grass Valley, California. The concentrates are made on vanners and are charged into a 20×4½ ft. Abbe tube-mill crushing in a 0.15 per cent KCN solution. The pulp from the tube-mill passes over amalgamation plates and then to classifiers, the spigot from which is returned to the tube-mill, while the overflow passes to tanks, where it is agitated mechanically. The period of agitation is six hours. During the treatment, the solution is twice decanted and replaced by a new solution. The pulp is then filtered in an Oliver filter. The concentrates treated contain from $30 to $40 per ton and an extraction of 93 per cent is made with a KCN consumption of 2½ lbs. per ton. The approximate cost of treatment is $3 per ton.

[10] *Loc. cit.*, 841.   [11] Mineral Industry. New York (1909), 361.

Other practises are described by Crosse,[12] Treatment of Ore Slime; Lindlay,[13] Notes on the Treatment of Mill Concentrate; and others.

GENERAL COMMERCIAL CONCLUSIONS.

The assays of the black sands have shown that a great loss of gold is taking place. The concentrates from the cleanup have a value which would pay for their cost of shipment many times over. Even after the most careful cleaning by the dredge, these concentrates frequently assay better than 100 pesos per ton.

A greater saving of the black sands can be made by more frequent cleanups. This also would result in a greater saving of the fine gold. Owing to the present arrangement of the tables, it is imposible to make a complete cleanup without shutting down the dredge. Some of the California dredges [14] have used a system by which the gravel is diverted to some of the tables, thus permitting a cleanup while in operation.

The present dredge does not utilize the full table area, and there is the possibility that another style of riffle would prove more effective in saving not only a large amount of the sands, but more of the fine gold as well. Powell [15] has recommended the carabou riffle as being very efficient.

Brazenall [16] has advocated the use of the Hancock jig to treat the dredge tailings of fine mesh. However, since the date of his writing, the Richards pulsator jig [17] has been placed upon the market and is in successful operation in many mills. The advantages of the Richards jig are: (1) Extremely small size, (2) very small power required, (3) small weight, and (4) small amount of water used. The possibilities of this jig, probably in combination with Wilfley tables, should be investigated.

Richards [18] has described a dredge having the following process: (1) Screen, (2) 30 coco-matting tables, (3) Wilfley tables, (4) amalgamation plates, (5) amalgamation cleanup barrel, (6) classifier, (7) amalgamation plates and traps, and (8) Wilfley

[12] *Journ. Chem. Met. & Min. Soc. So. Af.* (1909), 10, 172.

[13] *Ibid.* (1911), 12, 2 and 223.

[14] Aubury, *Bull. California State Min. Bur.* (1910), No. 57, 79.

[15] *Eng. & Min. Journ.* (1903), 83, 251.

[16] *Eng. & Min. Journ.* (1907), 83, 918.

[17] Shepard, *Eng. & Min. Journ.* (1909), 87, 545.

[18] Richards, Ore-dressing. New York (1906), 4, 1655.

table. The chief point for emphasis in this process is the continuous cleaning of the coco-matting tables.

Shipping direct appears to be the best present method of saving the values, though there is a possibility that magnetic treatment will give a greater profit. Amalgamation, with or without tube-milling, does not seem to be as economical as shipping. Cyanidation is probably out of the question in consideration of the small amount of black sands saved at present. Should the average black sands show much lower value than our lots, shipping direct would become unprofitable and magnetic treatment, or fine grinding, followed by amalgamation must be employed. The problem of the future is to save a much greater amount of these sands, then, even if the value is lower, cyanidation can be employed and a high extraction obtained.

NOTE.—Since the writing of this article, a number of changes have been made on the dredge. The screen has been replaced by two central chutes; only the pay gravel is run over the tables; the tables have been rearranged; and cleanups are being made only weekly. This has resulted in saving even less black sand than formerly.

ILLUSTRATIONS.

Magnified 10 diameters.

PLATE I.   NUGGETS FROM THE PARACALE PLACER DEPOSIT.

GEOLOGIC RECONNAISSANCE OF NORTHWESTERN PANGASINAN.

By Paul R. Fanning.

(From the Division of Mines, Bureau of Science, Manila, P. I.)

In 1911, northwestern Pangasinan came into a little prominence through the persistent reports of copper and other metallic deposits. Oil also was reported by prospectors to exist in vast quantities. In March and April a short geologic examination was made in order to confirm, if possible, the truth of these statements and to work out the general structure of the country. The latter is shown on a geologic map. The occurrences of copper, gold, silver, iron, manganese, and antimony were confirmed, but the known deposits appeared to be of no value. Evidence of oil or coal was not seen, although the formation is such as to permit of the occurrence of either.

GENERAL GEOGRAPHICAL FEATURES.

Location.—The area examined comprises about 350 square kilometers and is located in the northwestern portion of Pangasinan Province, Luzon, P. I. The region lies between the meridians 119° 45' and 120° 10' east longitude, and the parallels 15° 55' and 16° 20' north latitude, and is bordered on the west and north by the China Sea, on the east by Lingayen Gulf, and on the south by the Zambales Mountains. Manila lies 180 kilometers to the south.

Transportation.—The road from Dagupan to Lingayen, the capital of the province, is in perfect condition, but from Lingayen to Alaminos the road is passable to wagons during the dry months only. There are few roads in the remainder of the area, but during the dry season it is not difficult to traverse the country on horseback by means of the innumerable native trials. These permitted the examination of a large area within a short space of time.

Harbors are found at several places along the coast, particularly at Sual where there is deep, well-protected water.
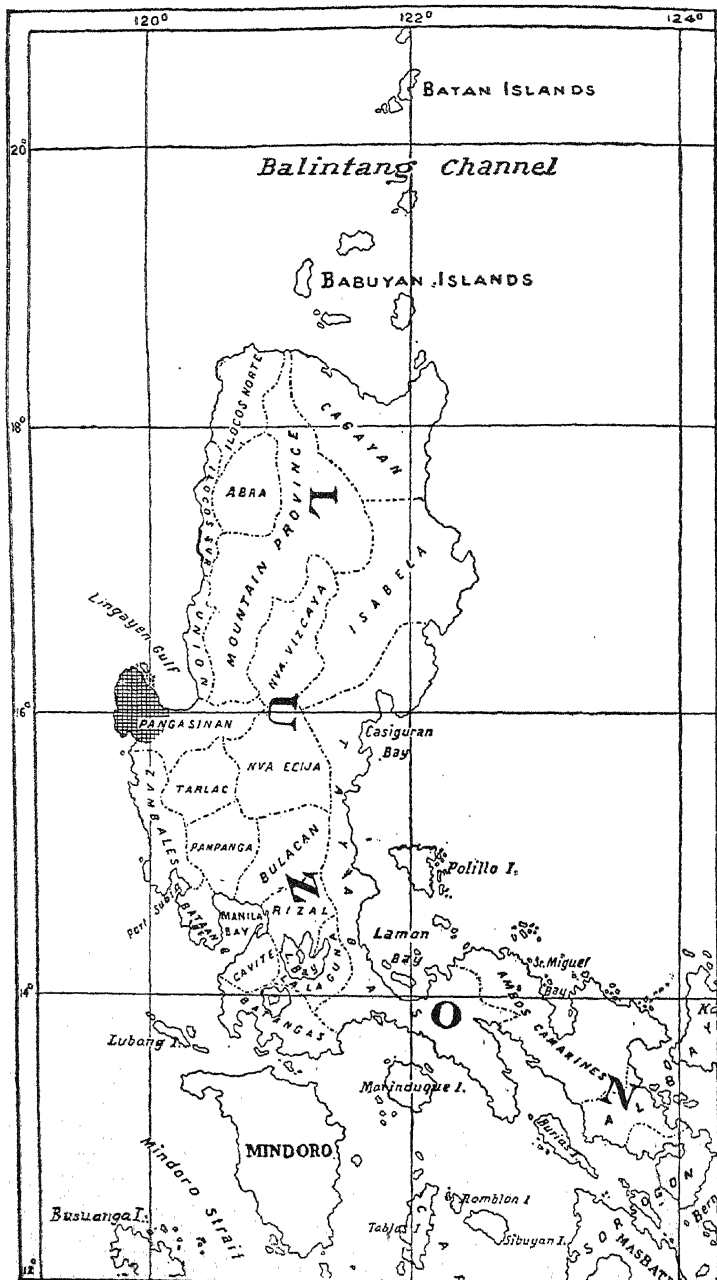
Fig. 1.—Showing area examined.

Relief.—The relief of the area is quite moderate, seldom reaching a height over 130 meters. The region, within comparatively recent times, has been gently uplifted above sea-level and erosion has subsequently cut out the various topographical forms. This uplift, as discussed later, began in the Pliocene age and possibly is even now taking place. The erosion generally is immature, and the majority of the rivers are incised in narrow sharp valleys which broaden into flood-plains just before entering the sea. A central sea-level river flood-plain occurs surrounding the municipality of Alaminos, and is flanked by hills to the east, south, and west.

The eastern range of hills extends from the southeast corner of the area northward to the sea and marks the termination of the Zambales Mountains. These mountains extend in a nearly unbroken line from the entrance of Manila Bay northward to the area.

In the southeast corner of the area, Mount San Isidro, elevation 890 meters, forms a prominent feature of the landscape. The shape of this mountain is somewhat conical with two conical points which apparently represent stocks of volcanic vents. From Mount San Isidro the hills decrease in altitude northward to the China Sea. This decrease is broken 5 kilometers from San Isidro by the central summit known as Verde Mountain, which rises to an elevation of 427 meters.

The southern hills spread out from the eastern hills and represent an uplifted formation now being deeply incised by river action. They embrace the headwaters of the Alaminos and Balincaguin Rivers, and are characterized by narrow valleys and precipitous slopes. The rivers are rapidly cutting cañons into the formations, and the side hills have not yet had time to round over into the more mature forms. Cliffs and buttes are frequently seen.

It is quite probable that the Balincaguin River began its eroding action in the Zambales Mountains before the more northern portion of the area emerged from the sea; and as the region rose, the river has continuously lengthened its course northwestward.

The western hills extend from the northwest corner of the area into the southern hills, and similarly represent an uplifted formation incised by river action. In form these hills are typically plateau-like, and their even sky-line is a marked feature of the topography.

Just west of Bani, the line between this plateau and the Alaminos flood plain is marked by a long scarp. This is in part due to river action, yet it is quite probable that part of the ero-

sion has been accomplished by sea-action, in which case it represents an uplifted shore-line.

Valleys.—With the exception of the Alaminos, all valleys are very narrow and deeply cut toward the source of the rivers, and gradually broaden into the flood-plains contiguous to the sea. The Alaminos flood-plain is the largest in the area and contains some 75 square kilometers.

Deltas.—The southwest corner of the area includes part of the great Agno delta which still is advancing northward into Lingayen Gulf. Drill holes put down at Dagupan and other places show many hundred meters of river silt.

The Dagupan well No. 32, bored in 1908, showed the following section:

Depth in feet.	Material.
0 to 40	Blackish sandy to stiff mud.
40 to 60	Fine gray sand, probably quartz.
60 to 184	Blackish mud with fragments of shells; pebbles at various depths.
184 to 189	Yellowish sand; stained by iron, probably by circulating water.
189 to 233	Blackish sandy to sticky mud with shell and a few pebbles.
233 to 328	Gray sand grading to finer sand containing some mud.
328 to 374	Blackish mud containing some shell and pebbles at various depths.
374 to 385	Gray sand, rather fine.
385 to 395	Blackish mud.
395 to 410	Gray sand with flow of water.

Deltas of large size are absent from the remainder of the area. Along the China Sea the rivers empty directly into the ocean where wave action has prevented delta growth.

Coral reefs.—Coral reefs, recent and living, fringe the shore-lines to-day as in the Pliocene. As in other parts of the Philippines, uplifted Pliocene coral may be traced from the land into the sea where the living forms are found.

Rivers and drainage.—The main drainage is northwestward along the Alaminos, Bani, Balincaguin, and Balingasay Rivers. The parallelism of the river courses is a feature structurally accounted for by the monoclinal northwest slope of the sedimentaries. Some minor drainage occurs southwestward down the Dasol River, and eastward down the east flank of the eastern range of hills.

The Agno River, one of the largest rivers in the Philippines, originates high in the mountains of north-central Luzon, flows southwestward to the great central plain of Luzon, then swings northward and empties into the ocean at the southeast corner of the region. All of the rivers, with the exception of the Agno,

are quite short and have small catchment areas. In spite of this and the small average flow, great changes are produced by periodical torrential storms. A heavy typhoon frequently produces a rise of from 5 to 10 meters in the larger streams, and the flooding of the sea-level plains is an annual occurrence.

Climate.—The climatic conditions have been studied by the Weather Bureau at Dagupan, a city some 16 kilometers east of the area and similar in its climate to Alaminos.

TABLE I.—*Meteorological data for Dagupan.*[a]

Month.	Rainfall.	Temperature.
	Mm.	*°C.*
January	15.2	26.1
February	28.5	26.6
March	43.6	27.1
April	49.9	28.5
May	309.9	28.1
June	326.9	28.2
July	504.1	26.9
August	413.9	27.1
September	276.5	27.2
October	235.9	27.2
November	89.8	26.5
December	11.5	25.6
Annual	2,305.7	
Mean		27.1

[a] Average data for a period of seven years furnished by Father Algué, director of the Weather Bureau, Manila, P. I.

Algué [1] states the facts as follows:

Absolute maximum temperature in 8 years 39°.5 C., minimum temperature recorded in same period 14° C. Range of temperature during the year 2°.6 C. Absolute range during 8 years 15°.2 C. Mean daily range during January 10° C., during September 8° C. There is a distinct wet and dry season lasting from the end of November to March. The percentage of rainfall during the months of June to October, popularly called the rainy season is at least 76 per cent of the total precipitation per year, while the rainfall from November to February never exceeds 12 per cent of the total average. April and May are apt to have more precipitation than the dry months owing to electric storms and occasionally, especially in May, to cyclones.

Population.—The inhabitants comprise Pangasinans and Ilocanos, of whom it is certain that the latter have recently spread out from the Ilocos provinces. The two languages are distinct and as yet have not had the time to produce a blend-

[1] An attempt to classify the climate of the Philippines, *Cablenews-American*, Yearly Review Number (1911), 53.

ing of words. The population centers in a few towns favorably situated along the rivers, and is increasing as would be expected in a sparsely settled region rich in agricultural possibilities. The municipality of Alaminos, which is the largest in the area, has a population of about 5,000 people. Anda, Bani, Sual, Dasol, Balincaguin, Agno, San Isidro, and Bolinao contain about 1,000 people each, and the remainder of the area is uninhabited except for a few scattered houses.

Cultivation.—Cultivation is entirely confined to the river valleys, especially the broad, flat flood-plain of the Alaminos-Bani Rivers, where the ground permits of the construction of large stretches of rice paddies. The usual clumps of coconut trees are seen, but these are cultivated on a scale barely sufficient to supply the local demand for nuts. Some tobacco is grown, but not nearly equal in amount to the local consumption.

The forests of Zambales spread northward into the southern part of the area, but the major part of the region is unforested. Sufficient mangrove fire-wood is cut near the seacoast to supply the local demand. A heavy growth of *cogon* [2] and *talahib* [3] grasses is generally found except in the cultivated valleys, and each year the natives burn this off for pleasure and to make travel easy. This custom is undoubtedly one of the reasons for the general absence of trees.[4]

Literature.—Roth [5] quotes Callery as stating that limestones exist in the area. This is the only known reference to the geology of the region. During the insurrection of 1898, the campaign was carried into the area and probably some United States Army records are in existence stating the general physiographic features of the country. The Coast and Geodetic Survey has published maps, numbers 4712 and 4209, in which the coast line is accurately plotted, but the locations given for some of the principal cities, rivers, and roads are in error.

GENERAL GEOLOGY.[6]

The rocks of the region comprise a basal igneous formation, later sedimentaries, alluvials, and coral. The field work was of such short duration and general character as would not permit of detailed study.

[2] *Imperata cylindrica* Beauv.

[3] *Saccharum spontaneum* L.

[4] Merrill, *This Journal, Sec. C* (1912), 7, 150.

[5] Roth, Justus. Ueber die geologische Beschaffenheit der Philippinen. In Jagor's Reisen in den Philippinen (1873), 340.

[6] Petrography by F. T. Eddingfield.

The basal igneous.—Igneous rocks are found at the northeast corner of the area and extend in unbroken line, southward and westward, and continue throughout the whole length of the Zambales Range. The formation is exceedingly complex, and affords a choice field for petrographic study. The parent magma has in the process of cooling differentiated itself into types varying in a series extending through granite, syenite, diorite, gabbro, and even to an ultra-basic, olivine rock. These have apparently cooled with varying rapidity and have given rise to finer-grained equivalents. As a much later phase of igneous activity, possibly wholly distinct, andesitic intrusion and extrusion took place.

Granite.—Granite, which is rare in the Philippines, is found near Pao Bay, near Sual, and on the Balincaguin River, 5 kilometers south of Barlo. It does not appear to occur over a large area, and wherever found was extensively intruded by andesite dikes. Its light color stands out in marked contrast to the generally black rocks of the region.

A medium-grained holocrystalline specimen from Pao Bay was seen in thin section to consist of quartz and feldspars with small amounts of intersertal ferro-magnesian materials. The feldspars are occasionally twinned in Carlsbad manner, and graphic intergrowth of quartz and feldspar is common. Small grains of magnetite are present.

A medium-grained specimen from Sual showed an inequigranular consertal fabric and was seen in thin section to consist of quartz, orthoclase feldspar, and hornblende. Some plagioclase and magnetite are present.

A porphyritic phase of the granite is shown by the specimen from south of Barlo. In thin section the rock has a seriate porphyroid fabric. The orthoclase shows inclusions of small feldspars and larger shreds of green hornblende. The groundmass consists of small prismoids of feldspar and irregular grains of quartz.

Syenite.—Syenites are far more rare in the Philippines than granites, yet both rocks were found at Sual and south of Barlo. In the latter place the syenite appeared to occupy a position between granite and diorite, and apparently indicates a mineralogical progression between the two types.

A variety from south of Barlo showed a medium-grained granitic texture. The rock is very hard, dense, and dark. In thin section the fabric is inequigranular, consertal, and the rock consists of orthoclase and light green hornblende. Medium-sized magnetite grains are quite numerous.

A variety seen at Sual on Portuguese Point showed an inequigranular porphyritic texture. The rock is very hard, dense, and not quite as dark as the variety just described. In thin section the rock shows a dosemic porphyroid fabric with phenocrysts of altered feldspar and pyroxene. Magnetite grains are abundant. The groundmass is entirely kaolinized.

In the syenite from Masbate, Iddings [7] found as accessory minerals, mica, apatite, chlorite, epidote, and secondary quartz. Apparently the mineralization is more diverse than in the case of Pangasinan. It is to be noted that magnetite is more abundant in the case of Pangasinan, and hornblende is present.

Diorite.—Diorite is probably an important rock of the region, although the specimens collected showed in most cases sufficient pyroxene to be classed as gabbros.

Gabbros.—Gabbros are found in abundance in the area of holocrystalline rocks from Sual northward, and also south of Barlo. The amount of hypersthene present would class many of these rocks as hypersthene gabbros or norites. The rocks are of granitic texture, of varying fineness, hard, dense, and mottled gray to black. In thin section the rocks generally exhibit consertal, inequigranular fabric, seriate to intersertal, and consist of hypersthene, pyroxene, plagioclase feldspar, and various minor minerals, hornblende, magnetite, etc. One specimen from south of Barlo consisted almost entirely of hypersthene and pyroxene and could perhaps be classed as a pyroxenite. This specimen showed extensive saussuritization of the few feldspars present. Some pyrite was noted.

Another specimen from south of Barlo showed pegmatitic structure and contained large crystals of plagioclase and light green hornblende besides abundant hypersthene. Decomposition and microscopical, replacement crystals were noted in this plagioclase. The pegmatitic structure of this rock was regarded with keen interest as it is the first specimen of this type (so abundant elsewhere) obtained in the Philippines.

Peridotite.—A peridotite was found on Portuguese Point, near Sual, and in hand specimen this rock is of granitic texture, hard, dense, and coal black. Under the microscope the rock appeared to consist nearly entirely of olivine which shows considerable alteration to serpentine. Some pyroxene and magnetite are present.

Andesites.—Dark porphyritic rocks, probably andesites, are

found over large areas and also as dikes within the coarser-grained rocks.

A specimen from the *barrio* of Cabulalwan, 4 kilometers north of Barlo, under the microscope, showed porphyritic, dopatic fabric. The phenocrysts were feldspar and hypersthene lying in a background consisting mainly of lath-like microlites of feldspar with intersertal serpentine. A dike rock from Pao Bay showed similar structure and mineralogy, but was very much decomposed. Another dike from the same locality was felsitic in texture and is probably andesitic in nature. The abundance of gabbros in the district would naturally suggest the presence of augite-andesites; that is, the fine-grained or porphyritic derivatives of the gabbros. These are known to occur abundantly in other parts of the Zambales Mountains and therefore are to be anticipated in Pangasinan.

Basalt.—A most interesting olivine basalt was found 4 kilometers north of Barlo. In hand specimen the rock is rather decomposed, is dark brown in color, and shows an amygdaloidal structure. Under the microscope the rock shows a porphyritic fabric with phenocrysts of pyroxene and olivine, the latter being greatly altered to serpentine. Amygdules, probably delessite, occur in large quantities filling vesicular cavities. They are generally spherical, but also occur in irregularly rounded and elongated shapes. The amygdules are made up of alternate light and dark shells of radial crystals with generally isotropic centers. In parallel light these shells show merely light and darker shades of yellowish brown, but under crossed-nicols they become subdivided into various colored bands with numerous isotropic ones. In some cases six separate shells were seen. The glassy background, adjacent to the amygdules, is frequently altered to give a surrounding ring of serpentine.

This is the first reported occurrence of delessite in the Philippines and Philippsite-bearing rocks (rare for the Philippines) in proximity makes the discovery all the more interesting.

Basalt is found along the Zambales Range, and specimens from Mariveles have been accurately described by Iddings.[5]

Tertiary sedimentaries.—Tertiary sedimentaries are found over the majority of the area, and extend in unbroken series from Barlo northward to the China Sea. The strata comprise tuffaceous marls, tuffaceous limestones, and water-laid tuffs. The strike is generally northeast with a slight monoclinal dip to

[5] *Ibid.*, 163.

the northwest. Horizontal bedding is frequently seen, and slight folding occasionally occurs. The beds are fossiliferous and have been referred to the Miocene. The country has been subjected to gentle uplift, and the formations have been elevated without disturbance and almost without folding. The beds are very soft, which shows that there has been no nearby igneous activity to metamorphose the strata.

The formation lies upon the northwest flank of the Zambales Range, and the contact with the igneous can be traced along the eastern and southern hills. The absence of metamorphism clearly shows that the sedimentaries are the younger. The igneous undoubtedly represents the Tertiary land mass around which the sedimentaries were laid.

Tuffaceous marls, shales, and clays.—The majority of the sedimentaries can be classed as tuffaceous marls or clays with varying calcareous content. The stone is generally soft, gray, and exceedingly fine-grained. Analyses of three specimens are given on page 278.

West of Bani the beds are beautifully exposed and comprise the western hills. The formation there has a slight dip northwestward to the sea with occasional gentle folding. Some beds are so low in calcareous content as to be named a shale or clay, and others are so high as to be classed as limestones. All appear to be more or less tuffaceous—a feature not visible in the hand specimens and unsuspected in the field. However, under the microscope, rock fragments were seen, which indicate a double origin.

It would seem that the deposition of the sediments, in part derived by erosion from the igneous land mass, was accompanied by the simultaneous inclusion of tuffaceous material, evidently from distant sources. The calcareous nature of the rock is probably due to the decomposition, possibly solution and precipitation, of the coral reefs which fringed the ancient shore line. Coral fragments and calcareous shell fragments are frequently found.

The following fossils were collected:[9]

Natica globosa Chemn.	*Dentalium tenuistriatum.*
Oliva (ancilla) sp.	*Arca* sp. indet.
Pleurotoma carinata Gray.	*Tapes* indet.
Morio echinophora Linn.	*Septaria arenaria* Lam.
Hindsia dyki Mart.	*Fusus* sp.
Flabellum sp.	*Turbo borneensis.*

[9] Determinations by Warren D. Smith.

These fossils assign the formation to the Miocene and Pliocene.

At Anda, Smith reports the beds as lying nearly horizontal, which would be expected from their similar position at the town of Bani, and found the following fossils: *Fusus* sp., *Morio echinophora* Linn., *Hindsia dyki* Mart. The reported existence of fossil elephant's teeth at this place could not be confirmed.

At Barlo, from where the sedimentaries extend across the length of the Alaminos Valley to Bani, the bedding shows folding, and dips as high as 30° northwest were recorded. The strike is generally north 30° east. At this place the contact with the ancient land mass can be seen and the relative age determined beyond question. The greater dip of the sedimentaries near the contact is in part due to the slope of the land mass, but in part it appears to be due to the uplift which slightly folded the beds at this place. In the process of uplift the greatest contortion is frequently found close to the land mass against which the pressure was directed. Along the Front Range of Colorado, U. S. A., the sedimentaries make a pronounced U-fold close to the contact and within a few miles flatten out into the horizontal beds extending across the Great Plains.

From Dasol, the sedimentaries extend southward along the west flank of the Zambales. South of Dasol, between Palauig and Santa Cruz, Von Drasche discovered a marl which is undoubtedly an extension of the Dasol marls. As stated by Martin:[10]

The occurrence of Miocene in the Philippines was first established by Karrer through investigation of Foraminifera which came from the western slope of the Sierra Zambales on the western coast of northern Luzon. There occur tuffaceous foraminifera bearing marls up to altitudes of 400 feet along the sea coast between Palauig and Santa Cruz and, perhaps still farther north. These marls are compared by Karrer with those from Java and elsewhere. He reached the conclusion that the marls in question are younger than certain Javanese beds which at that time had already been assigned to the Miocene, but he calls attention to the fact that the difference in age need not be considered so great as to necessitate assignment to different divisions of the Tertiary, since they probably represent only older and younger horizons. Accordingly Karrer correlates the marls of the Sierra Zambales as younger Miocene.

The foraminifera which appear to characterize the Palauig marls were not found in the few specimens collected from the beds near Dasol. However, their proximity, continuity, and

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[10] Martin, K., Sammlungen des geologischen Reichs-Museums in Leiden (1896), 5, 53–69. Translated by George F. Becker as a complement to his paper. *Ibid.*, 130.

equal age make the correlation quite certain. Referring to the Palauig beds, Adams [11] states: "This formation may correspond to the marine conglomerates which are found on the flanks of the southern portion of the cordillera." This correlation is not borne out by the writer's observations, for in studying the "marine conglomerate" at Patungon Bay and on Carabao Island, the discovery of hornblende crystals in the matrix indicated that the formation is distinctly of volcanic origin, thus confirming the belief of Becker and others. However, it is to be noted that the volcano was adjacent to the sea and the agglomerated lava was partly worked over to the formation of a conglomerate. The widespread tuffaceous activity contemporaneously taking place caused the intercallations of fine, water-laid tuff beds with the coarse agglomerate and conglomerate. The latter appears to be very local, of uncertain age, and to bear no similarity either in origin or lithology to the marls of Dasol, and so leaves no basis for correlation.

Martin [12] makes the suggestion that the Tertiary marls lying between Aringay and the China Sea can be correlated with the marls found by von Drasche on the west base of the Zambales. This correlation is made all the more exact by the now known occurrence of Tertiary marls in the intermediate Pangasinan area.

Tuffaceous limestones.—Limestones, probably tuffaceous, are found interbedded with the marls southeast of Alaminos and west of Bani. The rock is exceptionally white, and like the marls is very soft and fine-grained. Coral and shell fragments are frequent, and the strata evidently have been derived from the decomposition of the ancient coral. The limestone varies in composition, and in places is so earthy and impure as to be classed as marl. The texture is generally microscopically fine, though sometimes it is very coarse-grained, and 5 kilometers east of Dasol a bed was seen which was composed almost entirely of shell and coral fragments. This was found at the contact with the ancient shore line which accounts for the great abundance of shells. Coarse-grained limestones were never found distant from the old shore line.

Adams [13] questioned the occurrence of limestones in the Western Cordillera, but he did not visit the northern part of the

[11] *This Journal, Sec. A* (1910), 5, 71.

[12] Becker's translation, 130.

[13] *Loc. cit.*, 70.

Zambales Mountains and their general absence naturally led to such a belief.

Limestones have been found on the east side of the central plain of Luzon at Montalban and have been referred to the Miocene by Smith. Adams states that at Montalban, limestone and conglomerate are found toward the base of the series and are followed by shales, tuffaceous beds, and sandstones; these in turn are followed by limestone and variable clastic beds. This upper series appears similar to the formation in northwestern Pangasinan, and a corellation is indicated. It is to be noted that the extensive metamorphism of the Montalban beds is a point of contrast, and has resulted from the intense dynamic and igneous activities manifested along the west flank of the Eastern Cordillera.

Tuffs.—The sedimentaries, as noted, are of tuffaceous nature. However, they are distinctly different from the great tuff beds so characteristic of the coeval strata (the great Taal tuff) around Manila. The Manila beds consist almost entirely of volcanic ejecta, and the coarse fragmental character of the deposit is highly characteristic. The Pangasinan beds are of a more sedimentary nature, with admixtures of exceedingly fine scoriaceous material.

A study of the Zambales Mountains indicates that, during the period in which the Pangasinan sediments were being laid down, the volcanic activity of the range was confined to the central or southern portions. Owing to the distance, the ejecta, with the exception of the finer particles, could scarcely travel into the area. If the heavier particles had been carried northward by sea-currents, they would have lost much of their true character before final deposition.

It is probable that Mount San Isidro was active before the deposition of the sedimentaries now exposed by uplift. The aerial ejecta from these eruptions have either been eroded or else concealed by the later sedimentation.

In Tarlac Province, some 75 kilometers south of the area, andesitic tuffs are found on the east flank of the Zambales Range. These tuffs are water-laid, stratified, soft, gray in color, and fragmental in texture. Hornblende crystals are visible to the eye, and under the microscope the glassy groundmass is seen to contain numerous fragments of hornblende, tremolite, plagioclase, and magnetite. On the other side of the range, opposite this place, the tuffaceous marl mentioned on page 265 is found.

Martin[14] states that von Drasche found a range of hills near Aringay in which layers of tuff are exposed. Farther inland, von Drasche found the formation to be of a "hard, crystalline and sandstone" nature. On the other hand, Martin found the region to consist of marl rather than tuffaceous formations. I likewise found the strata to be more of the nature of true sediments, for at San Fernando conglomerates were found, and along the Naguilian trail, dirty, fine-grained sandstones were in evidence.

Radiolarian cherts.—Just north of Barlo,[15] chert boulders and slab fragments are found scattered over the surface of the ground, generally lying upon the marls. It is evident that the boulders have resulted from the erosion of the strata. The beds apparently are very irregular and limited.

In hand specimen the rock in certain types is exceedingly fine-grained and shows banded colors; red, brown, and gray. Under the microscope the thin section shows an isotropic ground-mass (probably chalcedonic silica) stained with hematite, and containing abundant, clear roundish areas which are doubly refractive under crossed-nicols. These clear spaces are believed to be casts of radiolarians from comparison with the radiolarian cherts of Ilocos Norte described by Smith,[16] specimens and slides of which are at hand.

Lawson[17] has spoken of the gradation, in radiolarian cherts, from sections "composed almost wholly of amorphous or isotropic silica to those which are holocrystalline aggregates or quartz granules."

Some of the Pangasinan cherts are of this holocrystalline type. The hand specimens are somewhat different from the first type as they are coarser-grained, and abundant white or yellowish-white quartz is present. This quartz is irregularly distributed in the specimen, often as a network of crystals, and occasionally filling vugs in the rock. Under the microscope the thin section is composed chiefly of interlocking granules of quartz (holocrystalline aggregates), often copiously stained with hematite, and containing magnetite and a few clear radiolarian casts. It was interesting to note that the quartz aggregates are secondary to the hematite stain, for blotches of this stain were seen in

[14] Becker's translation, 136.

[15] See Plate III, fig. 1.

[16] *This Journal, Sec. A* (1907), 2, 158.

[17] *15th Ann. Rept. U. S. Geol. Surv.* (1893–4), 420–426.

places to be cleanly fractured and the cleavages filled with the quartz.

Lawson in discussing the silica of the radiolarian cherts of the San Franciscan formation believed it to have originated from "siliceous springs in the bottom of the ocean." As stated:[18]

The hypothesis of the derivation of the silica from siliceous springs and its precipitation in the bed of the ocean in local accumulations in which radiolarian remains became embedded as they dropped to the bottom, seems, therefore, the most adequate to explain the facts, and there is nothing adverse to it so far as the writer is aware.

The above hypothesis appears strikingly applicable to the cherts of Pangasinan. Almost directly beneath the cherts, where the Barlo Creek cuts deeply into the underlying formations, the andesite has been extensively silicified by the action of circulating waters, and it would seem that during the deposition of the sedimentaries these waters discharged from the bottom of the ocean, and their silica content was deposited to the formation of the cherts.

Cherts recently have been found in many different parts of the Philippines such as Bulacan, Palawan, Mindoro, and Mindanao. All show great similarity, and it is possible that they may form an exceedingly valuable means of correlation. The cherts of Ilocos Norte were provisionally placed in the pre-Tertiary,[19] while the cherts of Pangasinan occur at the base of the Miocene-Pliocene formation. The provisional age determination of pre-Tertiary for the Ilocos Norte formation was made on a basis of similarity to the Mesozoic cherts of California, U. S. A., and the Moluccas; and in the absence of evidence to the contrary it is a possible supposition even though it marks the only pre-Tertiary formation as yet found in the Philippines. Concerning the field relations of the Ilocos Norte cherts it is stated that:[20]

"It is exceedingly limited in its outcroppings and quite variable in its phases, never being encountered as a continuous formation but only as isolated outcrops which reveal little or nothing as to its position." Concerning the paleontological evidence it is stated, "as yet I have been unable to make any specific determinations from these slides."

It is positively known that, during the Tertiary, siliceous springs were very active throughout the length of Luzon. This is shown by the quartz veins which are found in numerous places

[18] *Ibid.*, 424.
[19] Smith, *This Journal, Sec. A* (1910), 5, 319.
[20] Smith, *This Journal, Sec. A* (1907), 2, 158.

along the cordilleras and which are especially abundant at Paracale, Benguet, and Bontoc and can be traced northward into Ilocos Norte. These veins are almost without exception confined, or genetically related, to igneous intrusives or extrusions of Tertiary age. The age determination is positive owing to the intrusion of Tertiary sedimentaries.

The Ilocos Norte cherts are probably the work of siliceous submarine springs,[21] and it is to be suggested that possibly these belonged to the great Tertiary period of spring activity manifested throughout the Philippines. It is also to be remembered that the geology of Ilocos Norte is quite similar to the geology of northwestern Pangasinan—indeed, they are not far distant along the same coast of Luzon—and it seems more natural to compare these, rather than to make the comparison with California. It is to be noted that the Pangasinan cherts lie at the base of the Miocene sedimentaries, which is in striking conformity with the probable occurrence of the formation in Ilocos Norte.

Conglomerates.—Conglomerates were not found in the area and it is a singular fact that they have not been found anywhere in the Zambales Mountains with the exception of the so-called "marine conglomerate" of Manila and Olongapo Bays, to which reference has already been made in this paper.

Conglomerates are so characteristic of basal beds, and are found in such abundance along the adjacent, parallel, Eastern Cordillera of Luzon as to raise a question as to their real absence and, if such is true, the cause of this absence.

Coral.—Uplifted Tertiary coral is found following the contact between the basal igneous and the sedimentaries; that is, they follow the old shore line. The coral does not occur as a large mantle covering the country, as it does in Cebu and some other regions, but is found as isolated cliff-bound mesas 10 to 30 meters high. The coral, because of its superior hardness, is resistant to erosion, and acts in many cases as a hard cap to the underlying sedimentaries. Recent coral, as noted under topography, is found along the present shore line, and is similar to types abundantly described by others.

STRUCTURAL GEOLOGY.

The area comprises the northern extremity of the Zambales Cordillera and marks the termination of the tectonic line extending from Mariveles (near Manila) northward through

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[21] Smith, *ibid.,* 159.

Bataan, Pampanga, Zambales, Tarlac, and Pangasinan Provinces, a distance of about 150 kilometers. The rock types over this area show great similarity and the geologic history is practically identical.

Within the area, the basal igneous formation can be divided into rocks of two ages. The older rocks generally are coarsegrained and consist mainly of gabbro and diorite along with granite, pyroxenite, and periodite. Large areas of fine-grained or porphyritic rocks occur, andesites and basalts, and it is possible that part of these may be hypabyssal phases of the same magma. The exact nature of the formation is a matter of speculation owing to the complete absence, as far as known, of the original rock into which the magma was intruded. The widespread similarity of the plutonic rocks in the Zambales Range certainly suggests that the magma was of batholithic size and nature.

The age of this great intrusion is almost certainly pre-Miocene, and the majority of writers have placed the basal igneous of the Philippines in the pre-Tertiary. Becker has stated:[22]

From early Paleozoic times onward an archipelago has usually marked the position of these Islands. The diorites and associated massive rocks may have made their appearance about the close of the Paleozoic.

The occurrence of dikes in many parts of the area shows that igneous activity was renewed subsequent to the solidification of the magma.

Mount San Isidro in the southeast corner of the area is of volcanic shape (though greatly eroded), and the felsitic to porphyritic character of the surrounding rocks also indicates its volcanic nature. Most of the andesites of the adjacent area probably represent lava flows originating from this volcano, although these flows apparently were massive in their character as beds are conspicuously rare. The age of this volcanic activity is probably late Tertiary.

The tuffaceous sedimentaries lay upon the basal igneous and were deposited in the Miocene-Pliocene sea subsequent to the lava flows, although some distant volcanic activity must have been taking place during the period of deposition. The structure of the sedimentaries, as a whole, is monoclinal with a dip of 0 to 10° northwestward to the China Sea. Variations in the strike and dip show that a slight amount of folding has taken place. Mashing and faulting apparently are absent. No intrusions were noted in the sedimentaries, and it is very likely

that in the area examined none exists. The sedimentaries can be found to an elevation of at least 100 meters, and the uplift probably was not much greater. This small uplift is in contrast with the position of correlative beds in the Central Cordillera of Luzon where elevations of 1,600 meters occur. The upheaval of Pangasinan and the Zambales Mountains is still taking place as proved by uplifted recent coral.

Alluvials.—Alluvials are found in the hills only to a limited extent, as the stream erosion does not permit the formation of thick beds. The base-level valleys, as around Alaminos, are covered by beds of river silt, due to the periodic floods.
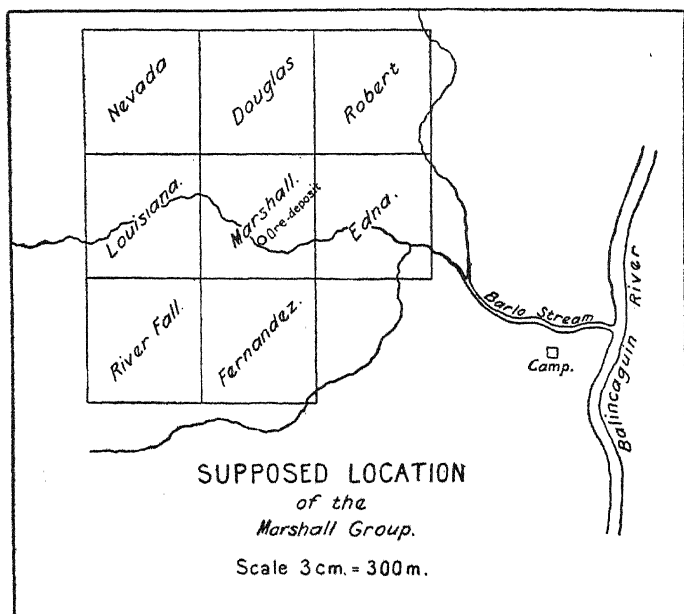
FIG. 2.—Supposed location of the Marshall group.

ECONOMIC GEOLOGY.

ORE DEPOSITS.

Gold.—The region exhibits few of the features characteristic of gold deposits. Quartz veins are seldom seen, placers seem absent, and the rivers pan only the minutest traces of gold. Natives have done no mining worthy of mention, and for the Philippines this is strong confirmation of the nonexistence of ore deposits.

The major portion of the region is covered with a considerable

thickness of recent sedimentaries. These sedimentaries have not been metamorphosed nor intruded by dikes; they probably possess little gold, but even on the assumption of its presence, apparently there have been no active waters to produce concentration into ore-bodies.

Along the eastern and southern hills, igneous rocks make up the major part of the formation; hence, they can be considered favorable places for the occurrence of veins. Indeed, all veins within the region actually do occur within this igneous complex.

North of Sual a quartz vein was noted on the Levant claim
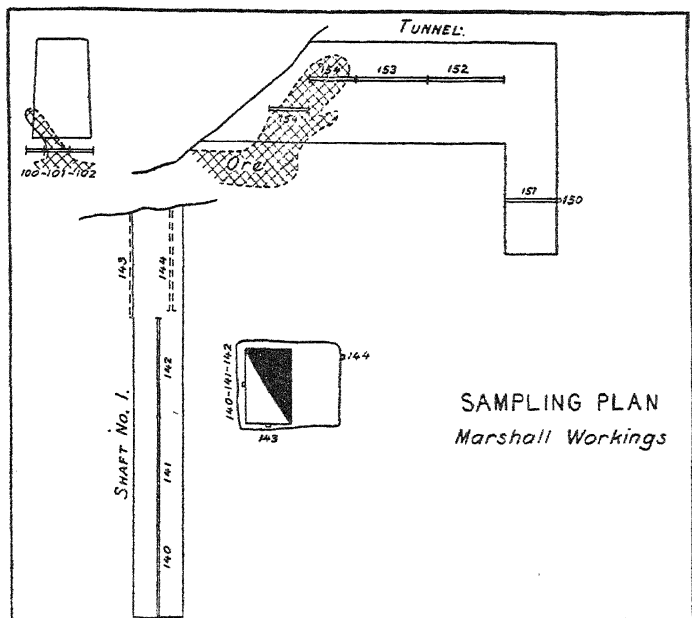
FIG. 3.—Sampling plan, Marshall workings.

which appeared to be about 1 meter wide. The vein is poorly exposed, but seems to be of the fissure type. Some pyritization and silicification of the walls have taken place, but gold values appear to be absent. Assays of the vein showed 2 per cent copper.

At Barlo on the Marshall group of claims, extensive silicification of the country rock has taken place. The formation is andesite, and, by the action of siliceous waters circulating along fractures, considerable alteration of the rock has taken place. This silicified zone was mistaken by prospectors for an enor-

mous vein, "a mountain of ore," but the assays show neither gold
nor silver.

On the Napoleon claim, near Malipagao Mountain, 5 kilome-
ters south of Barlo, a small vein was noted which, however, had
no appearance of continuity. Assays showed no valuable metals
except a small percentage of copper. The nearby Union claim
also showed a few quartz stringers, but values apparently are
absent.

North of Barlo, numerous boulders and slabs of chert and
jasper were found, lying on the surface of the ground. Were

SKETCH

Showing Plan of Workings
and Occurrence of Ore-body
on the Marshall Group.

Scale ½ in = 3 feet.

▨ Cupriferous Pyrite.

▧ Basalt.
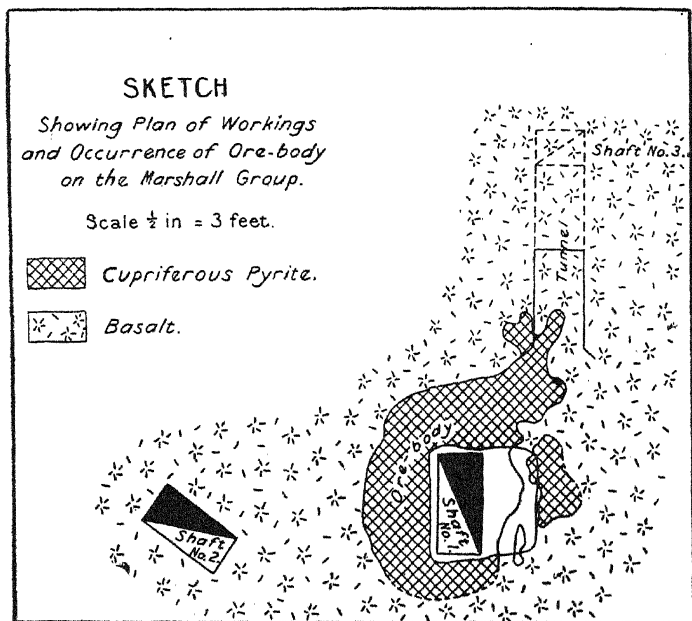
FIG. 4.—Plan of workings and occurrence of ore-body.

these boulders in a region of better transportation facilities,
they would serve very well for tube-mill pebbles in the cyanide
mills of the Philippines.

In further prospecting for gold, silver, or copper, the search
should be made farther south in the Zambales Range along the
main body of the igneous formation. There the conditions are
favorable for vein formation, and it is quite probable that future
work will discover their location.

Copper.—Copper is found on the Marshall claim at Barlo, on
the Napoleon claim south of Barlo, and on the Levant claim north

of Sual. On the Marshall claim the copper is associated with
pyritic lenses in the silicified fractures mentioned under gold.
The origin of these lenses is not altogether certain, but their
occurrence indicates that they have resulted from the shattering
of the zone and the work of circulating waters. It is to be noted
that pyrite occurs disseminated throughout much of the andesite,
and its origin there is purely primary as an original crystallization
from the magma. Faint traces of copper can be detected in this
disseminated pyrite. Immediately surrounding these lenses, the
andesite has been decomposed into a clay. This undoubtedly is

N-S.-SECTION
of
Workings on Marshall Group.
Scale ½ in. = 3 feet.

Cupriferous Pyrite.

Basalt.
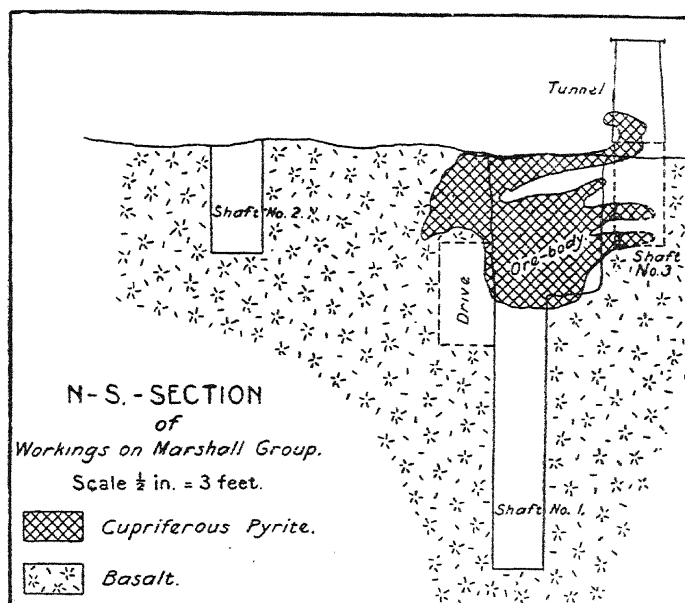
FIG. 5.—North-south section of workings on Marshall group.

due to the oxidation of the pyrite, forming acidic waters which
attacked and kaolinized the surrounding rock. The occurrence
of gypsum and calcite crystals is indicative of this reaction.

The lenses were sampled and analyses revealed copper, a little
gold, antimony, and zinc. The gold is associated with copper in
chalcopyrite; the antimony is combined with the copper in the
mineral tetrahedrite; and the zinc occurs as sphalerite. The last
mineral often occurs as black crystals lining cavities in the py-
rite, and its occurrence there is purely secondary. As shown
by Plate IV, a little prospecting work has been done on the

property, and altogether some 50 tons have been developed. However, the costs of mining, shipping, and smelting are so high as to preclude the possibility of profit. The shaft and tunnel were sampled, and the results of the assays are shown in Table II.

TABLE II.—*Assay of samples taken on the Marshall workings.*[a]

Sample No.—	Gold per ton.	Silver per ton.	Copper per ton.	Remarks.
	Pesos.		*Per cent.*	
100	none	none	trace	
101	trace	none	6.0	
102	none	none	trace	
140	none	none	none	
141	none	none	none	
142	none	none	trace	Zinc present.
143	1.24	trace	15.6	Zinc present.
144	none	none	0.5	
150	nouc	none	none	
151	none	none	none	
152	none	none	trace	
153	none	none	trace	
154	none	none		
Dump clips	1.60	trace	8.8	Antimony and zinc present.
Shaft grab	1.24	trace	9.7	Zinc present.

[a] For position of sample numbers see the sampling plan on page 723.

Iron.—The Camagsinala iron claim lies 5 kilometers west of Sual on the Alaminos road, and was stated to contain a "vast deposit of high grade iron ore." Investigation showed the formation to be andesitic, covered by the usual tropical iron-stained soil, and the only evidence of iron ore was a few scattered grains of magnetite and hematite which have resulted from the decomposition of the andesite. The deposit is of no value.

Manganese.—One of the features of the reconnaissance was the examination of the manganese deposit. The specimens previously submitted to the Bureau of Science for analysis were so high in manganese content as to warrant close investigation.

The deposit is located on the north end of the Marshall group of claims at Barlo, and was found to consist of a few boulders and numerous pebbles and grains of psilomelane and pyrolusite strewn over the ground. The deposit is residual, and has resulted from the decomposition of the sedimentaries or andesite, and subsequent concentration along gullies. The higher specific gravity of the manganese compared to that of the andesite has made this concentration possible. Analysis of one specimen gave the following results:

TABLE III.—*Analysis of manganese.*[a]

Constituent.	Per cent.
Manganese (Mn)	[b] 58.58
Iron (Fe)	0.55
Phosphorus (P)	0.100
Alumina (Al)	0.38

[a] Analyzed by T. Dar Juan.
[b] Equivalent to 92.5 per cent manganese dioxide (MnO_2).

This shows an excellent grade of manganese ore, but the deposit is so superficial and limited as to be of no commercial value.

While it is obvious that the ore has resulted from the weathering of the rock, its occurrence and origin there is not yet known. The fact that the manganese is found on the surface of the ground adjacent to the line of fracture and close to the cherts suggests that the submarine springs which produced the cherts were the agencies which brought the manganese to the sedimentaries or andesite. Analysis of the cherts revealed the presence of manganese and it is possible that the precipitation of the silica was accompanied by the simultaneous precipitation of the manganese.

It is impossible to state where the springs originally obtained the manganese, but it is feasible to assume that the waters percolating through the andesite dissolved some manganese in passage. A striking example of this process was seen in the water flowing into Taal Volcano subsequent to the eruption of March, 1911. This water in passing from the lake surrounding the volcano through the andesite forming the sides of the crater gained in manganese content from a trace to 79.9 parts per million.[23]

NONMETALLIC DEPOSITS.

Road-building material.—At San Isidro in the southeastern corner of the area, a quarry was opened for the extraction of the andesite for road construction. This rock was used on the road from Dagupan to Lingayen which is known as one of the best roads in the Philippine Islands. The quarry was abandoned upon completion of the Lingayen road, but will probably be reopened when more road-metal is required. The quarry is located on the Agno River close to the sea, and might be considered a source of metal for the streets of Manila. However, the cost of transportation and the uncertainty of smooth water during much of the year make this seem unfeasible.

[23] Cox, Alvin J., *This Journal, Sec. A* (1911), 6, 96.

Oil.—The greater part of the region is covered by a great thickness of fossiliferous, tuffaceous sedimentaries, and the structural conditions are favorable to the possibility of oil. However, no evidence of its actual presence was seen. During the wet season it is said that a heavy film of oil occurs on the surface of the water, that seepages in the strata have been seen, and that the smell of gas is very distinct. It is said that the oil has been so abundant at times as to destroy crops, and it is stated that one year burning oil spread over the Bani River and was carried to the sea.

The examination of this region in the dry season revealed no trace of oil, and the more recent examination[24] in the wet season also failed to discover any indication. An artesian well, now being bored at Alaminos, has reached a depth of over 250 meters, but no evidence of oil has been found.

Cement material.—The great tuffaceous marl deposits around Abu and west of Bani contain beds which appear to be well adapted to the manufacture of Portland or other hydraulic cement. This is shown by the following analyses:

TABLE IV.—*Analyses of cement materials.*[a]

Constituent.	1	2	3	4
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Silica (SiO2)	68.68	46.13	44.76	0.38
Alumina (Al2O3)[b]	11.62	23.13	14.23	0.18
Iron oxide (Fe2O3)[c]	5.90	7.51	7.60	trace
Calcium oxide (CaO)	2.85	10.38	15.72	55.62
Magnesia (MgO)	0.79	0.66	3.65	0.00
Loss on ignition	7.16	13.19	13.92	43.50
Ratio of SiO2 to Al2O3+Fe2O3	3.9	1.5	2.1	0.2

[a] Analyses 1, 2, and 3 by T. Dar Juan, division of general, inorganic and physical chemistry; analysis 4 by Alvin J. Cox.

[b] Approximately.

[c] Total iron determined as ferric oxide.

Sample 1 came from sedimentary beds just west of Bani. The texture is very fine-grained and no grit can be felt under the fingers. The chemical analysis indicates a shale or marl. In thin section under the microscope, the rock shows a glassy structure, rounded grains of magnetite are abundant, and fragments of decomposed feldspars are numerous. The rock is tuffaceous in character.

A free-sand determination gave the following results:

[24] Made by Warren D. Smith.

TABLE V.—*Free-sand determination on Sample No. 1.*[a]

Constituent.	Per cent.
Feldspar	75.09
Silica (in feldspar)	61.21
Silica (soluble)	7.94
Total silica (SiO_2)	69.15
Alumina $(Al_2O_3$ in feldspar)	13.88
Silica (In quartz and feldspar)	61.12
Quartz feldspar	75.00

[a] Analysis by Forrest B. Beyer, division of general, inorganic and physical chemistry. This analysis was approximate and may vary from 1 per cent to 2 per cent. Free sand was absent.

Sample 2 came from the sedimentaries at Abu and was taken from near the bottom of a well 3 meters deep. In hand specimen the rock is light gray, and exceedingly fine-grained except for a few minute fossils. The rock effervesces with acid. The chemical analysis indicates a marl, and under the microscope the rock is seen to be tuffaceous in character. A thin section shows an exceedingly fine-grained rock with glassy structure. Occasional grains of magnetite and fragments of tremolite and feldspar are present. The minerals are much decomposed and under crossed-nicols the slide is mainly isotropic except for innumerable tiny stars of doubly refractive, crypto-crystalline minerals, probably feldspars. The magnetite is somewhat decomposed.

Sample 3 came from a small knoll at Abu, within 0.5 kilometer of sample 2, and represents the same horizon. In appearance and under the microscope this sample is similar to sample 2.

Further analysis of sample 3 showed the following:

TABLE VI.—*Analysis of Sample No. 3.*[a]

Constituent.	Per cent.
Soluble silica in hot hydrochloric acid	0.65
Soluble silica in sodium carbonate	15.70
Silica as free sand	1.53
Total silica	undetermined
Sulphur	0.10

[a] Determined by T. Dar Juan according to specification of Bleiniger, Ohio State Geological Survey.

As indicated by the intercallations seen in the field, variations of high and low silica and calcium are revealed by analysis. The average is low in calcium, which deficiency could be met by the use of coral from the elevated reefs of Alaminos or south of Balincaguin. The purity of this coral is shown by analysis No. 4.

Mr. W. C. Reibling [25] states:

Samples 3 and 4 can be combined to form an ideal mixture for the manufacture of Portland cement. Considering first their chemical composition we find that a mixture of one part of sample 3 and 2.2 parts by weight of sample 4 will produce cement clinker of the following composition:

Constituent.	Per cent.
CaO	65.6
SiO_2	21.7
Al_2O_3	7.0
Fe_2O_3	3.7
MgO	1.7

According to European standards the hydraulic modulus should be about 2.0; that is, the content of calcium oxide should be twice as great as the sum of the percentages of silica, alumina, and ferric-oxide; the permissible variations ranging from 1.8 to 2.2. The hydraulic modulus of this mixture is exactly 2.0. Also, this mixture calculates almost identically with the formula obtained from the average American Portland cement, the latter being 1.10 CaO, 0.363 SiO_2, 0.074 Al_2O_3, 0.021 Fe_2O_3 (allowing for the presence of 0.83 per cent CaO as sulphate), and the former 1.1 CaO, 0.363 SiO_2, 0.116 Al_2O_3, 0.060 Fe_2O_3.

The ratio of silica to alumina is 3:1. This ratio and the presence of a desirable quantity of fluxing material (3.7 per cent of Fe_2O_3) guarantees easy burning, the very small percentage of MgO (1.7) insuring no trouble from that source.

Considering next the physical condition of these two materials, we find that they are both fairly soft and very finely grained; therefore, they can be ground into an impalpable powder at a low cost. The argillaceous material is free from irregularly distributed matter such as concretionary nodules of ferrous carbonate, calcium carbonate, etc., and would require a minimum amount of chemical work and would be an easily controlled raw mixture.

The formation occurs in great thickness and is well adapted to easy quarrying. The analyses made are so favorable as to warrant further sampling and investigation. The splendid transportation facilities which can be developed in the Pangasinan area may make this region of merit equal to that of the other regions of the Islands now being investigated as possible sites for cement plants.

[25] Chief, division of general, inorganic and physical chemistry, Bureau of Science.

ILLUSTRATIONS.

Fig. 1. View of Sual Bay, looking northward.
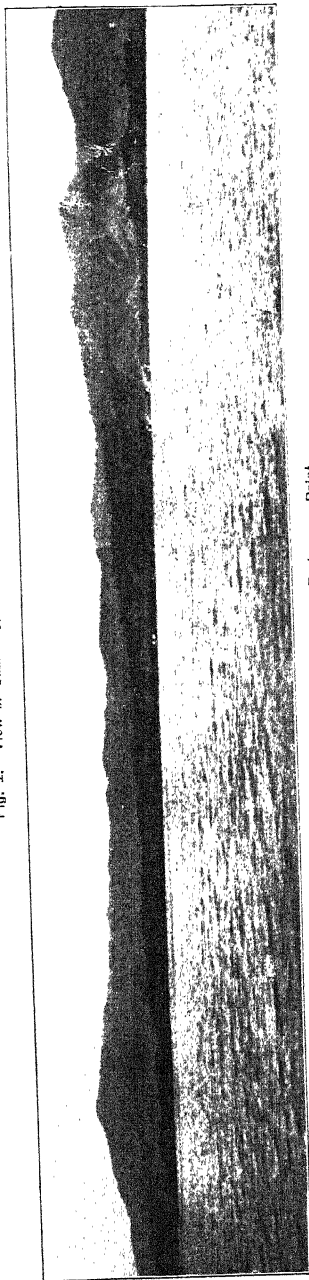
Fig. 2. View of Sual Bay from Portuguese Point.

PLATE I.
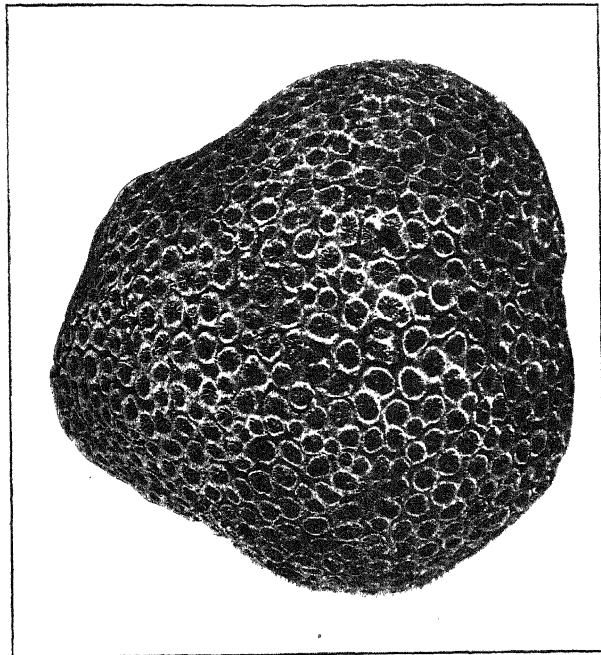
Fig. 2.   Coral.

Fig. 1.   *Heliastrora* sp. from ridge 5 kilometers east of Dasol.
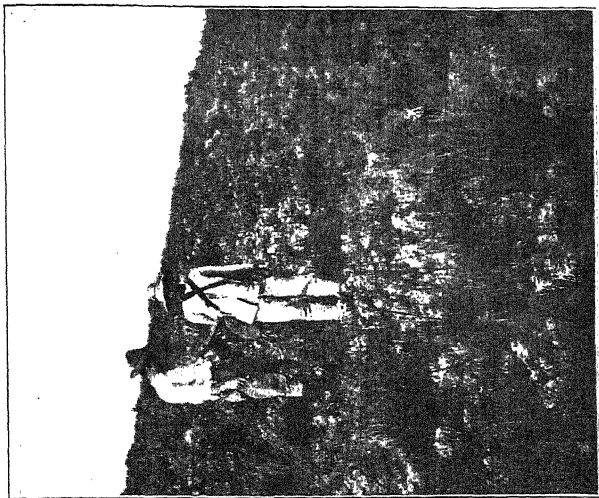
PLATE II.

Fig. 1. Chert boulders.
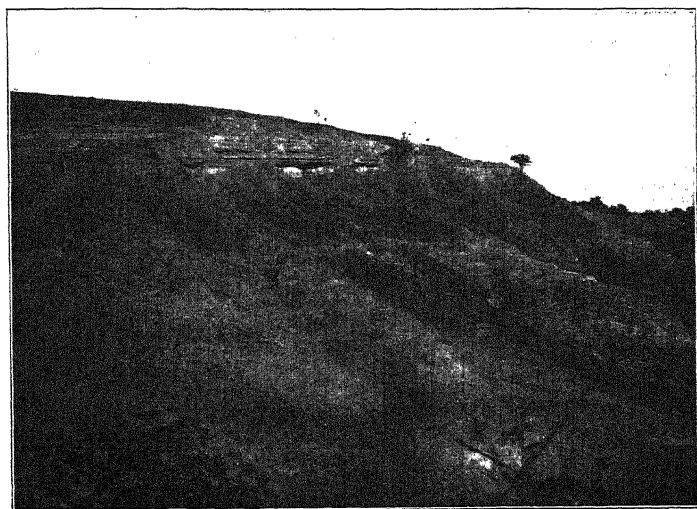
Fig. 2. Tuffaceous limestone west of Bani.

PLATE III.

Fig. 1.   Marshall tunnel; ore showing to left.

Fig. 2.   Marshall shaft; ore showing on surface.

PLATE IV.

L I N G A Y E N   G U L F

SECTION A—B.

SECTION C—D.

GEOLOGIC RECONNAISSANCE MAP OF NORTHWESTERN PANGASINAN LUZON
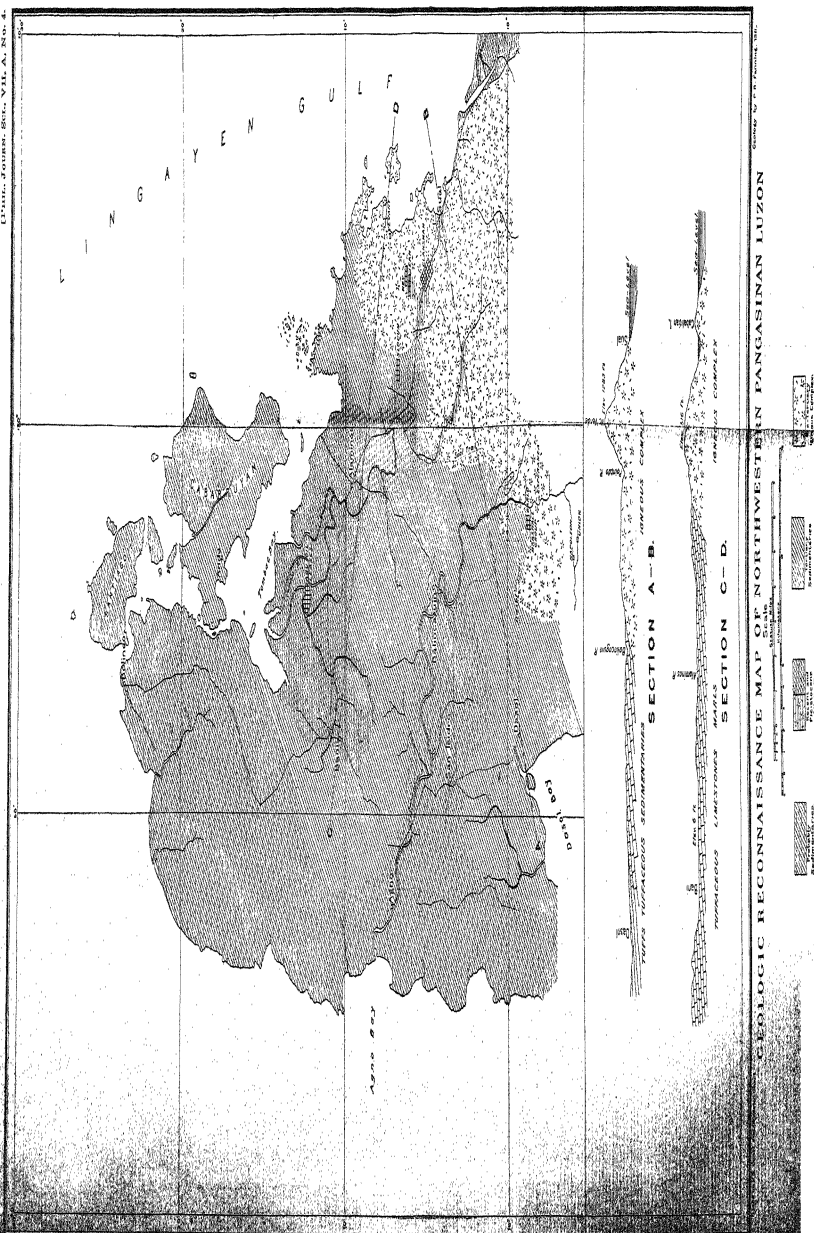
TIMOR ISLAND; ITS SUPPOSED VOLCANO AND ITS PROBABLE TECTONIC RELATIONS.

By GEORGE I. ADAMS.

(*Professor of Geology, Pei Yang University, Tientsin, China.*)

Timor Island is situated in the eastern part of the Moluccas. This group shows certain trend lines which are in part well defined. In the western part, the "Java line" is marked by a close alignment of islands bearing volcanoes. In the eastern part, where the position of the islands is not so regular and there is a break in the chain of volcanoes, several interpretations have
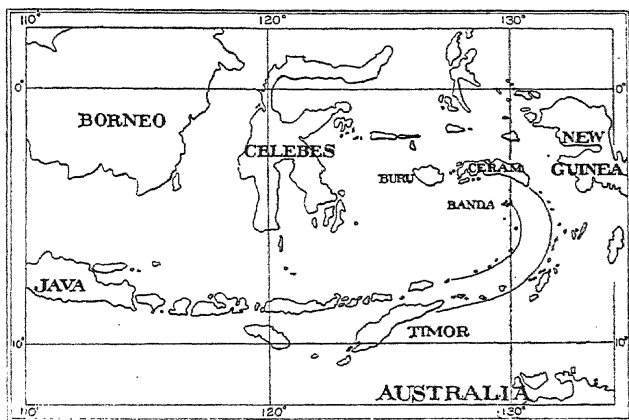
FIG. 1.—Timor and neighboring islands.

been offered as to the tectonic relations. Timor is one of the islands concerning which there has been uncertainty.[1] The following notes may serve to a clear understanding of its relations in the group.

In September, 1910, I visited Timor for the purpose of examining some occurrences of oil and gas. Before going to the island, I tried to inform myself concerning its geologic consti-

[1] Cf. Suess, Das Antlitz der Erde. English translation, The Face of the Earth, 3, 241–243; 4, 309.

tution. The literature available to me in Manila, where I was stationed, yielded little definite information, the most conspicuous statement being that Timor contains a volcano. Consulting Scrope's work, which contains the earliest catalogue of volcanoes which is generally referred to, I found the following statement made in connection with the discussion of the destruction of volcanic mountains by explosion:

Such a catastrophe destroyed in the year 1638 a colossal cone, called the Peak, in the Isle of Timor, one of the Moluccas. The whole mountain, which was before this continually active and so high that its light was visible, it is said, three hundred miles off, was blown up and replaced by a concavity now containing a lake.

In another passage the destruction of the cone of Timor is mentioned as a case supporting the "engulfment theory," and in the catalogue the addition is made that the volcano once served like Stromboli as a lighthouse.

Although I questioned the possibility of the light of a volcano being visible at a distance of 300 miles, and wondered who of the early mariners might have used it as a lighthouse before the eventful date of 1638, it did not occur to me that there would be any difficulty in finding the ruins of the "colossal cone." Shortly after my arrival in Dilly, the capital of the eastern part of the island which belongs to Portugal, I began to inquire concerning the volcano, but no one knew of such a volcano as I asked about. One of the officials told me of a "mud volcano," but I found no one who had seen it. Thinking that the "mud volcano" might be a solfatara near the formerly active center, I planned to visit it.

On arriving at Viqueque, which is near the south coast of Timor and southeast of Dilly, the local Portuguese official in response to my inquiries obtained a guide and we set out to see the place which was well known to the natives. After riding for about an hour and a half down the river valley in which Viqueque is situated, we came to a place east of the river mouth and near the beach. There we saw what had once been a mud cone about 100 meters in diameter and 15 meters high, judging from the crescent-shaped eastern portion which indicates its former dimensions. The western part of the cone has broken down and spread in several nearly concentric mud flows. In the center of the crater there were two small cones less than a meter in height, which looked wet; the surface around them was deeply cracked mud. I ventured on it, although a stick thrust into the cracks reached soft mud at a shallow depth. A small amount of muddy water was rising from the centers of the cones, just about enough to balance the loss due to evaporation and to keep the sum-

mits wet. An occasional bubble of gas broke in the rising mud, and I found that by shaking myself I could communicate a vibration to the mud-cracked surface and cause bubbles to appear in rapid succession. The gas proved to be inflammable. Our guide, who was an old man, stated that he had seen the mud volcano in activity and that it made a noise and had a flame which gave a light visible from Viqueque. He could not tell the date of the eruption, but said that it was many years ago. This seemed evident from the growth of small trees near the spot. I think it is probable that there have been several eruptions of the mud cone, some of which may have resulted from "excitement" during the periods of violent earthquakes which have occurred since its formation. The successive mud flows accord with this idea.

A few days after leaving Viqueque, I met Dr. Frederic Weber of Geneva, Switzerland, who has examined oil properties at Polaca. He had traveled in the western part of Portuguese Timor, and he assured me that he had seen no signs of recent volcanoes. He kindly showed me a copy of an article by Dr. Hans Hirsch [2] who had made notes on the geology along practically the same route which I had traveled, but following it in a reverse direction. Hirsch described the mud cone near Viqueque and ascribed it to a gas eruption. He stated its location as being 7 kilometers southeast of Fato-Hada which, according to his map, is the same village which I have called Viqueque.

A careful search of the literature on volcanoes shows that most writers in speaking of Timor have followed substantially the statements made by Scrope, but with some errors in transcribing the date. Mercalli,[3] however, makes some additional statements. He says:

The volcano of the island of Timor made a grand explosive eruption in 1638, another violent explosive eruption occurred at the volcano Floan-Bano in the western part of Timor the 26th of December, 1856; finally a third eruption took place in the volcano Bibiluto in May 1857 (Perrey).

In a footnote he cites Scrope in reference to the eruption of 1638 and adds:

In 1856 two people were killed by stones hurled out by the volcano of Timor. The eruption of 1857 was accompanied by a strong earthquake and a fissuring of the ground which caused the death of 36 people (Perrey). Probably all these eruptions should be referred to one volcano which bears different names.

[2] *Neues Jahrb. f. Mineral., Geol. u. Paleon,* 24, Beilage Band, 160.
[3] G. Mercalli, I Vulcani Attivi Della Terra, 313.

Bonney [4] is the only author I have found who appears to discredit the accuracy of the statement reported by Scrope. He gives no references, but says:

The Java line is continued * * * to Timor, in which the existence of volcanoes has been doubted; there must, however, be a very few for one in the western part of the island is said to have been in eruption in 1856 and in the following year; there are also some mud volcanoes, but nothing calling for special mention.

Finally, in Schneider's catalogue of volcanoes, [5] Floen Bano is given as the name of the volcano of Timor, its latitude and longitude are stated, the dates of eruption are noted as 1638, 1856, and 1857, and its location is shown on a map as being in the eastern part of the island, although Mercalli has stated that Floen Bano is in the western part.

The writings of Perrey to which Mercalli refers may be either "Notes on Earthquakes" [6] or two special articles which he wrote; the first [7] proving to the author's satisfaction that there is certainly one volcano on Timor and the second [8] showing that there may be another.

It seems reasonable to conclude, however, that Perrey was led into error through a lack of knowledge of the local geography and geology and by assuming that the incidental mention of "volcanoes," in an untechnical report by the governor of Portuguese Timor describing earthquakes, was sufficient proof of the existence of volcanic phenomena. For example: the 36 people reported killed in 1857 were on Pulo-Camby which is a small island north of Timor. Perhaps the fact was overlooked that Pulo means island, and, failing to note this, the fatalities were thought to have been in Timor.

The statement, "The volcano of Bibiluto erupted with extraordinary violence and destroyed a part of the village of the (native) kingdom of Viqueque" may be interpreted as a report of two results of the seismic disturbance which were confused into a local cause and effect. I believe that the "mud volcano"

[4] Bonney, T. G., Volcanoes, their structure and significance (1899).

[5] Schneider, Karl, Die Vulkanischen Erscheinungen der Erde (1911).

[6] Perrey, Alexis, Note sur les Tremblements de Terre en 1857, avec suppléments pour les années antérieures (see pp. 34 and 90). Extrait de Tome X des Mémoires couronnées et autres Mémoires in 8°, Académie royale de Belgique.

[7] Perrey, Alexis, Sur le Bibiluto, Volcan de l'île de Timor, Nouvelles Annales des Voyages, August (1858), 129.

[8] Perrey, Alexis, Deuxième note sur les phénomènes seismiques à Timor, ibid., Décembre (1858), 303.

which I have described as situated near Viqueque is the so-called volcano of Bibiluto of this report. It may have "erupted" as a result of earthquakes which also caused damage in Viqueque. However, it should be noted that there is a reference in earlier writings, which Perrey cites,[9] to a volcano "en ignition" situated in the native kingdom of Bibiluto. This may reasonably be explained as another gas vent, since it is a well-known fact that there is an occurrence of oil and gas in Bibiluto on the south coast of the western part of Portuguese Timor, but according to my informant there is no such mud cone there as is found near Viqueque.

The original publication concerning the so-called eruption of Floen Bano is evidently a note published in the Javasche Courant, May 9, 1857, as is shown in the article to which Perrey refers and which consists of a number of notes concerning earthquakes. It reads as follows:

The 26th or 27th of December, 1856, the mountain Iloen Bano in the western part of Timor erupted causing the death of two persons struck by stones which the volcano threw out. The account from which we are borrowing these details is all the more remarkable since it is the first notice of an eruption of a volcano in Timor, or at least in the western part of the island.

(It will be noted that the name has been misspelled by Mercalli and also by those who have taken their information from him.) It is my opinion that this is another case in which earthquake phenomena have been misinterpreted and ascribed to a volcanic eruption.

I was pleased to find in Perrey's article "Le Bibiluto" a reference [10] to what is probably the original source of the statements made by Scrope concerning a volcano in Timor. The literal translation from the Latin is as follows:

There was also, in the island of Timor, a mountain so high that its flaming summit was said to be visible three hundred miles at sea. In the year 1638 when its foundations were shattered by a terrible earthquake, together with the island, it was absorbed, leaving only a great lake in its place, as the annals of the Society of Jesus record.

It is useless to conjecture as to what may have been the basis for this statement. It may be remarked that the later statements which have been made on the strength of this passage show certain variations and additions which give them in the connection in which they appear greater apparent scientific

[9] M. de Freycinet, Voyage de l'Uranie, part hist., pp. 536, 546, et 566.
[10] Th. Ittig, De Montium incendiis, Lipsiae, 1671 in 8° voy., p. 120.

value than the original would warrant. Especially is this true since the later statements carry with them the weight of scientific authority. In this case, as in the preceding ones which have been discussed, there is no testimony from an eye witness, and the statements made contain no internal evidence that they are based on the observation of phenomena of volcanic eruptions. Moreover, the examination of the island has not yet brought to light any evidence of volcanic activity during historic time.

The geologic formations of Timor in so far as they are known consist of igneous and metamorphic rocks, with younger Paleozoic, Triassic, Jurassic, and younger Tertiary sedimentaries. The younger Paleozoics and Triassic formations have been broken by igneous rocks, but the Jurassic and younger Tertiary have not been seen to be so, or to show contact metamorphism. Timor has not been well mapped, but it has been sufficiently explored so that recent volcanic phenomena would not have passed unnoticed. Evidently it should not be included in the list of volcanic islands. The "Java line" which has been traced into Timor by some authorities passes to the north of Timor and terminates in a hook-like curve which extends through the Damar Islands to the Banda group. Timor belongs in an outer curved line which swings around through Timor Laut, the Lesser Kei Islands, Ceram, and Buru which, in so far as known, have similar geologic formations and do not contain volcanoes.

ILLUSTRATION.

EDITORIAL.

A PHILIPPINE NATURAL BRIDGE.

In July of 1910, while making a geological reconnaissance in the vicinity of Silang, Cavite Province, P. I., the writer discovered a natural bridge of unusual size, and owing to its remoteness it is probable that the place had not previously been visited by white men. It is noteworthy that this is the first large natural bridge reported in the Philippines, although it is likely that future explorers will find others, especially in the great bedded tuff area lying between Manila and the Gulf of Tayabas where the rock is favorable for their formation.

The bridge is on the Lucsuhim stream about 3 kilometers west of the *barrio* of Silang, and 50 kilometers south of Manila. It can be reached from Silang by following the Silang-Indang road for about 3 kilometers, to the *barrio* of Lucsuhim and then striking northwest across the fields for about 2 kilometers until the cañon of the Lucsuhim stream is reached. The opening under the bridge span is tunnel-like and has a diameter of about 10 meters and a length of about 75 meters. It makes a double turn that roughly approximates the shape of the letter S. During low water the stream occupies a central channel consisting of a staggered series of small falls and potholes which are the result of the action of the water upon the horizontal bedding of the tuff rock.

The floor of the bridge, which is about 40 meters above the stream, was examined and showed evidence of once having formed the bed of the stream. Erosion has nearly obliterated this old bed, but it has not been sufficient to destroy the sides of the valley. At one time the river must have flowed at this higher elevation to a place several kilometers down stream from the present tunnel and then passed over a cliff. This cliff gradually receded upstream forming the present box-cañon. As illustrated by the sketches (fig. 1), seepage began at a point several hundred meters above the falls and, owing to the horizontal bedding of the rock, it first took a path at right angles

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Stage 1. *Water-fall.*

50 m.

Stage 2. *Seepage begins. Water-fall partly drained.*

Underground Connection

Stage 3. *Water-fall becomes extinct. Caving begins.*

Stage 4. *Present Condition. Caving advanced.*
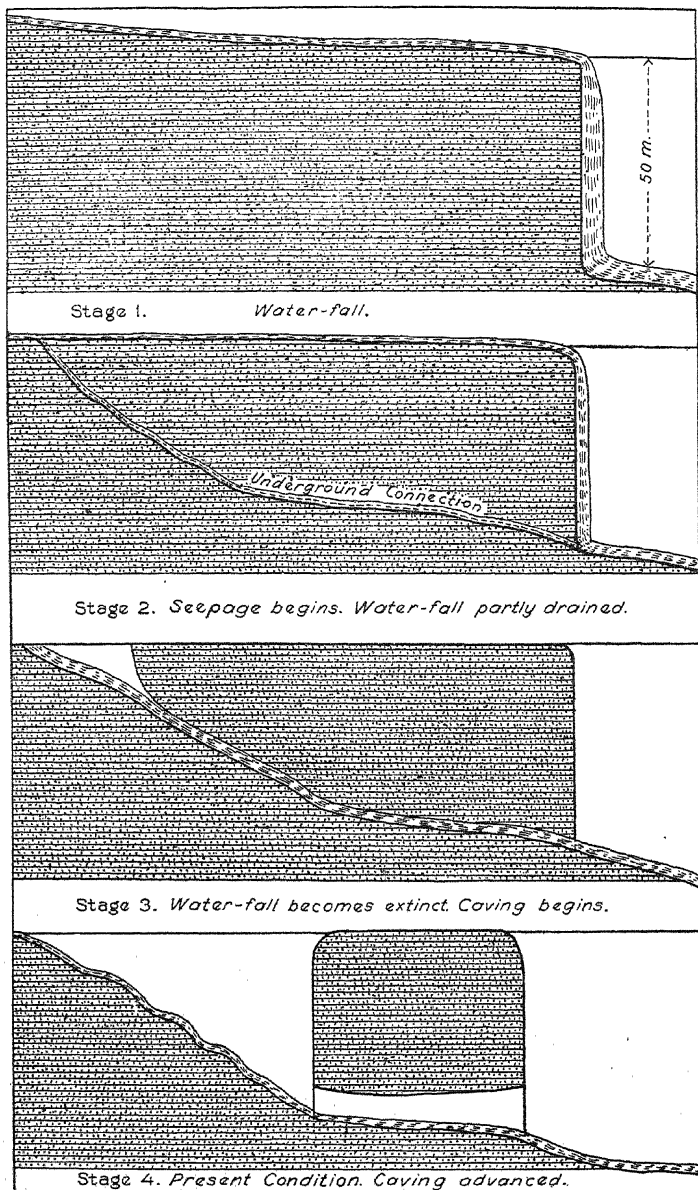
FIG. 1.—Illustrating the formation of the natural bridge.

to the river course, then descended from bed to bed to the bottom of the falls. The porous, soft nature of the rock favored the rapid enlargement of the underground channel, and eventually the entire stream followed this course.

Subsequent erosion and caving have greatly decreased the length of the underground channel and produced the short cañon above the present entrance portal. Owing to the thinness of the roof, the first part of the tunnel caved rapidly, whereas the erosion and caving of the lower part was much slower. A condition now has been reached where the entrance and exit portals will be eroded with about equal speed and at the same time the tunnel will be greatly enlarged in diameter by down cutting and by caving of the roof. Under these conditions the bridge eventually should assume the arch structure characteristic of famous natural bridges in other parts of the world.

PAUL R. FANNING.

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ILLUSTRATION.

THE OXIDATION AND DETERIORATION OF COAL.[1]

By ALVIN J. COX.

(From the Division of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.)

Owing to the necessity of storing coal and to the fact that it is being stored in increasing amounts from year to year, it appears desirable to investigate the changes which take place when coal is exposed to the air. Probably the most notable of these changes is the direct addition of oxygen, and it is this with its accompanying reactions which I desire to discuss. When one considers the comparative uniformity of the composition of coals, it is not surprising that the capacity to absorb oxygen should be a common property. On the other hand, there is a decided difference between the kinds of coal, and the rate and amount of the oxygen absorption partly depends on this factor.

The literature is full of extravagant statements concerning the results of the exposure of coal to atmospheric conditions, yet much reliable data has been published on this subject, and the idea is generally accepted that a change occurs in bituminous and lower grades of coal which is of sufficient magnitude to make it of industrial significance. But the economic importance of the ever-present, slow oxidation of coal is probably underestimated, and much additional investigation must be carried on before we shall arrive at a complete understanding of all the factors which influence the deterioration of coal. It seems un-

[1] Read before the section on Fuels and Asphalts, Eighth International Congress of Applied Chemistry, September 4–13, 1912, Washington and New York.

desirable in this paper to discuss the literature of the subject in detail, and I shall confine myself chiefly to the results of my own experimental work, the study of which I began in 1908. I have selected samples of coal for my investigation from some of the best sources in the Philippines.

Sample No. 1 is a coal from the military reservation, Batan Island, several tons of which were shipped in sacks direct from the mine to the Bureau of Science for a steaming test. During the test, 100 kilograms were collected, a shovelful at a time, and from this a small sample was secured by quartering and reducing the size of the pieces to that of a small marble. A 2-liter glass-stoppered bottle was completely filled from the sample and the air excluded. This was reserved for experimental purposes.

Sample No. 2 is from Polillo and was taken by me from a pile of 16 tons which had lain in an open bunker for a year. The sample was prepared and kept as described for No. 1.

Sample No. 3 is from Camansi vein No. 2, near Danao, Cebu. The coal was shipped in sacks from Cebu soon after being mined direct to the Bureau of Science for a steaming test. The sample was taken and bottled as described for No. 1.

Sample No. 4 was brought to the laboratory from Bulalacao, Mindoro, in a sack. This coal was sampled as described above.

Sample No. 5 came from the mountain district of Luzon and had been stored in sacks in our warehouse for one and one-half years, when it was sampled for these experiments in the same manner as the others.

At the beginning of the experiments, each sample was carefully worked over to remove noncoal particles, cracked until all pieces would pass a sieve having 2 meshes to the centimeter (5 meshes to the inch), and that portion which would pass a sieve having 4 meshes to the centimeter (10 meshes to the inch) was discarded. It was then looked over again, grain by grain, to see that no earthy matter or lint was intermixed. The samples were made as uniform as possible. All these operations were carried on in the air. For each experiment a sample was quartered from the bulk sample, so that all results are comparable in this respect. All analyses were made according to standard chemical methods, and especial care was exercised to maintain uniform conditions. In the determinations of the calorific value, the same Berthelot-Mahler bomb calorimeter was used throughout and the temperature differences were determined by the use of a Beckmann thermometer. I have made a water correction of the results by subtracting 6 calories for each per cent of water. All

corrections are comparable, and I believe that irregularities in the samples and manipulation could not have produced errors of any consequence.

Two 250-gram samples of each coal, one in air and the other in oxygen,[2] were stored for about nine months in 7-liter bottles at about 30° C. in an ordinary room lighted by diffused sunlight. The bottles were stoppered with rubber stoppers through each of which passed two glass tubes by means of which the gas samples were taken. Fresh air was frequently supplied with a bulb to those bottles containing air. The small size of the coal particles offers a greater surface in proportion to the mass and thus facilitates the absorption of oxygen. Analyses of the samples before and after storage are as follows:

TABLE I.—*Analyses and calorific values of Philippine coals stored in air and oxygen respectively.*

Coal No.	Original sample.					After storage in air.			After storage in oxygen.		
	Moisture.	Volatile combustible matter.[a]	Fixed carbon.	Ash.[b]	Calories.[c]	Moisture.	Ash.	Calories.	Moisture.	Ash.	Calories.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*		*Per ct.*	*Per ct.*		*Per ct.*	*Per ct.*	
1	5.90	46.30	40.08	7.72	6,159	5.59	7.52	6,119	5.75	8.11	6,059
2	8.61	40.67	46.55	4.17	6,012	8.75	4.50	5,931	8.08	4.25	6,022
3	11.55	37.43	46.95	4.07	6,066	11.11	4.47	5,985	11.18	4.20	5,982

[a] After the method of Cox, *This Journal, Sec. A* (1907), **2**, 41.

[b] Each analysis shows somewhat less ash than the ordinary coal from the same source because of the way in which the samples were prepared.

[c] Average of three closely agreeing, independent determinations.

The above calorific values are not comparable as they stand, since the samples contain different quantities of diluents (water+ash).[3] When they are calculated to an ash- and moisture-free basis, coal—(water+ash), we then deal with alterations in the pure coal substance, and the results show that in each case the calorific value is lowered by storage as given in the following table:

[2] Ordinary commercial oxygen, free from carbon dioxide, 91.5 per cent of which was absorbed in alkaline pyrogallol, was used. The bottles were alternately partially evacuated and filled with oxygen from the bomb, until the gas left in the bottles was practically commercial oxygen.

[3] This does not represent the original amount of ash with its hydrated silicates and with its iron pyrites instead of ferric oxide formed by burning [Parr and Wheeler, *Journ. Ind. & Eng. Chem.* (1909), **1**, 636], but the same coal burned to ash in the same way unquestionably gives concordant results.

TABLE II.—*The deterioration in calorific value of coals stored in air and in oxygen.*

Coal No.	Calorific value of the pure coal.			Lowering of calorific value.	
	Original sample.	After storage in air.	After storage in oxygen.	Stored in air.	Stored in oxygen.
				Per cent.	Per cent.
1	7,130	7,042	7,034	1.2	1.3
2	6,893	6,836	6,865	0.8	0.4
3	7,189	7,089	7,069	1.4	1.7

The gases above the coal at the end of the storage period were analyzed as follows:

TABLE III.—*Composition of the gases above the coals stored in air.*[a]

Coal No.	Volume percentages.		
	Carbon dioxide.	Oxygen.	Remainder.
1	1.5	18.7	79.8
2	0.2	17.7	82.1
3	1.3	15.8	82.9
4	2.2	15.9	81.9
5	3.2	15.7	81.1

[a] The gases above the coal were frequently replaced with air freed from carbon dioxide to insure an adequate supply of oxygen. Therefore, these results do not show the total amount of carbon dioxide evolved, but show its presence and the exact composition of the gas above each coal when it was removed for analysis.

TABLE IV.—*Composition of the gases above the coals stored for nine months in commercial oxygen.*

Coal No.	Volume percentages.		
	Carbon dioxide.	Oxygen.	Remainder.[a]
1	6.0	22.9	71.1
2	1.6	19.5	78.9
3	2.6	14.2	83.2
4	4.5	17.9	77.6
5	4.9	14.4	80.7

[a] Unabsorbed in alkaline pyrogallol. Traces of carbon monoxide were detected, but hydrogen, methane, formaldehyde, formic acid, or hydrogen peroxide were not recognized by ordinary means of identification as reaction products, although it is probable that some or all of them were present in small quantities.

The glass tubes carried by the rubber stoppers of the storage bottles were closed with rubber tips which, as well as the stoppers themselves, deteriorate so rapidly in a tropical climate that it was impossible to keep the bottles tight. The analyses indicate that as fast as oxygen was absorbed by the coal it was replaced by air. The bottles which contained the coal stored in oxygen were refilled with oxygen after they had been sampled for the analyses of Table I, and after fifteen months the composition of the gases above the coal samples was as follows:

TABLE V.—*Composition of gases above coal in second stage of storage in oxygen.*

Coal No.	Volume percentages.		
	Carbon dioxide.	Oxygen.	Remainder.
1	14.6	42.9	42.5
2	10.3	39.8	49.9
3	25.7	29.1	45.2
4	14.4	30.7	54.9
5	63.0	7.2	29.8

These results show further deterioration of the coal samples, and, taken with those of the next preceding table, indicate that the evolution of carbon dioxide is not simultaneous with the absorption of oxygen, but is subsequent to it.[4] It is possible that a number of oxidation processes varying in character and speed of reaction are involved, depending on the kind of coal, the stage of the process, etc., but the facts are satisfactorily explained by the assumption that oxygen is absorbed by the unsaturated chemical compounds of the coal to form organic peroxides, and carbon dioxide is evolved when the peroxides break down.[5] In cases of autoxidation, hydrogen peroxide has been frequently met with, and it is probable that in the autoxidation of coal the organic peroxides may be hydrolyzed slowly by water to form

[4] Porter and Ovitz, *Journ. Am. Chem. Soc.* (1908), 30, pt. 2, 1489, note that some coals rapidly absorb oxygen from the air surrounding the coal during storage without forming carbon dioxide; however, the maximum duration of their tests was one hundred four days and from their own numbers the content of carbon dioxide began slightly to increase after thirty-four days. Also *idem*, *Journ. Ind. & Eng. Chem.* (1910), 2, 80, "Coal absorbs oxygen from the air during storage without forming carbon dioxide and the amount of oxygen absorbed accords approximately with the deterioration in heat value."

[5] Brooks, *This Journal, Sec. A* (1910), 5, 219, offered this hypothesis to explain the oxidation of Manila copal by the air.

hydrogen peroxide which reacts upon the coal to produce carbon dioxide.

There is a marked increase in the weight of Philippine coal when exposed to the air, although no definite quantitative determinations have been attempted on account of the fluctuation of the moisture content. Absorbed gases could reduce the calorific value of coal by simply adding weight to it; that is, they would be merely a diluent. However, if oxygen on being absorbed enters into the composition of the coal or unites with the carbon or hydrogen of the coal, there is actual deterioration. When pure coal becomes oxidized, the total weight and the total heating value are decreased without changing the calorific value of what remains.

The avidity with which coals absorb oxygen is shown by the following experiments. Samples of 100 grams each were sealed in glass bulbs in an atmosphere of air or oxygen as indicated. After a period of twelve months the pressures were measured and the gases analyzed as follows:

TABLE VI.—*Analyses of residual gases, when coal is stored with relatively small amounts of oxygen.*

Coal No.	Stored in—	Diminished pressure.	Volume percentages of the gases after storage.		
			Carbon dioxide.	Oxygen.	Remainder.
		Mm.			
1	air	123	5	0.4	94.6
2	oxygen	504	75	0.0	b 25.0
a 3	air	106	7	0.0	. 93.0
3	oxygen	600	59	0.0	b 41.0
4	air	70	13	0.0	87.0
5	oxygen	167	92	0.0	b 8.0
c x	air	120	8	0.0	92.0

a Vein No. 3.

b This is accounted for by the inert gas in the commercial oxygen.

c From the East Batan Coal Company mine.

The above numbers show that the absorption of oxygen by coal is complete when an insufficient supply of the former is present.

An apparatus to measure the rate of absorption of oxygen by coal, which consists of a barometer for measuring the pressure within a hermetically sealed space, was devised and constructed as shown in fig. 1.

The portion a b d e was made of capillary tubing and then at a sealed on to an ordinary 100-cubic-centimeter glass pipette f. The tube b c is about 800 millimeters long. The apparatus was inverted, the coal sample inserted through the wide tube g which was afterward sealed in a gas flame and allowed to cool, and finally the apparatus was returned to its upright position. The heavy rubber tubing, d h, is of sufficient length to allow free movement of the mercury vessel i over the distance b c. The vessel i was partially filled with mercury and then lowered below c. The apparatus was alternately partially evacuated and filled with commercial oxygen (6.4 cubic centimeters not absorbed in alkaline pyrogallol) at e until the gas left in f had practically the above composition. The vessel i was next raised until the mercury in it was level with that in the tube c e, and the difference in height of the mercury in c b and c e noted. Simultaneous barometric and temperature readings were always made, and from these the exact gas pressure in f was calculated. The samples used in all of the foregoing experiments had been exposed to the air for some time previous to the beginning of the experiment. The deterioration, which unquestionably begins with the mining of the coal, consists in the loss of combustible gases, and oxidation already must h a v e progressed considerably; therefore, the amount of oxidation found by the analyses is not nearly as great as it would have been if the measurements had been begun
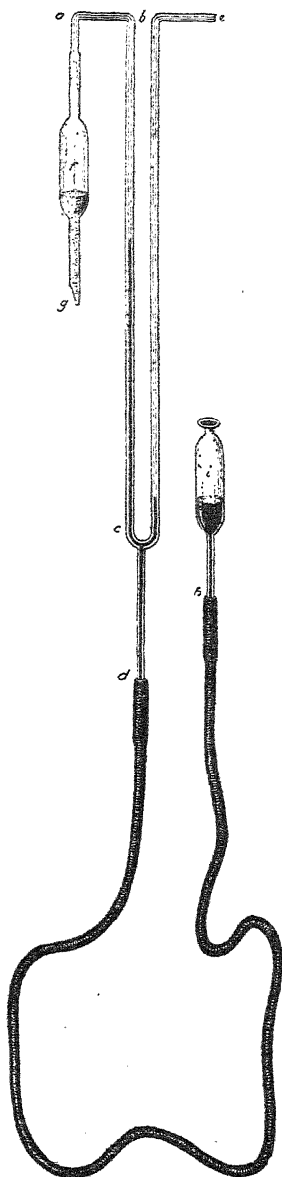
Fig. 1.—Apparatus to measure the rate of absorption of oxygen by coal.

with fresh samples. Therefore, a sample from a new face of the coal from the mine of the East Batan Coal Company was secured for the following absorption experiments and brought to the laboratory in a sealed container. A portion of the sample was ground to pass a sieve having 2 meshes to the centimeter (5 meshes to the inch) and graded into the following sizes:

Portion.	Passed sieve.		Held on sieve.		Weight of fraction.
	Meshes per cm.	Meshes per inch.	Meshes per cm.	Meshes per inch.	
					Grams.
A	2	5	4	10	2,005
B	4	10	8	20	1,080
C	8	20	24	60	735
D	24	60	40	100	50
E	40	100	60	150	50
F	60	150	----------	----------	75

Analyses of these portions are as follows:

TABLE VII.—*Analyses of portions of a Philippine coal passing sieves of different sizes.*

Portion.	Constituent.					Color of ash.
	Moisture.	Volatile combustible matter.	Fixed carbon.	Ash.	Total.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
A	22.82	33.64	39.04	4.50	100.00	Dark brown.
B	22.37	34.32	38.33	4.98	100.00	Yellowish brown.
C	23.04	33.28	38.66	5.02	100.00	Yellowish brown.
D	22.51	33.32	38.34	5.83	100.00	Yellowish brown.
E	21.85	33.19	39.15	5.81	100.00	Dark brown.
F	21.96	33.67	37.77	6.60	100.00	Dark brown.

The relative rate of the absorption of oxygen was obtained for a 20-gram sample of each of the following: namely, A quickly ground in a mortar which I will designate AA, A, C, E, and F when each was placed in a piece of apparatus like that shown in fig. 1. About two hours were required to crush, sift, and weigh the portions and samples, except AA, and to exhaust, seal, and begin the actual measurements. The results are as follows:

TABLE VIII.—*The comparative avidity of coal particles of different sizes for oxygen at 30° C.*

Time after starting.		Diminished pressure in millimeters.				
		AA	A	C	E	F
Days.	hrs.					
0	18	270	109	270	253	165
0	26	326	147	333	273	224
0	42	399	191	407	355	295
3	0	460	251	472	452	363
4	0	495	313	505	493	406
5	0	514	343	520	505	422
7	0	521	400	551	516	456
10	0	519	452	523	507	454
36	0	503	544	501	485	447
365	0	477	518	456	462	386

It is easily seen from the above table that with each coal the pressure diminishes for a time and then increases. The reduction in the pressure was due to the gradual absorption of oxygen by the coal, but in time the rate of the evolution of carbon dioxide was equal to that of the absorption of oxygen, and later even exceeded it and thereby increased the pressure. These observations substantiate the assumptions made in considering Tables IV and V, that the evolution of carbon dioxide is subsequent to the absorption of oxygen.

The absorption of oxygen by A, the coarsest sample, after sealing is not very rapid; but that by C, which is very much finer than A, is two and one-half times as fast. Sample AA is the same portion as A, but was quickly pulverized in a mortar immediately before beginning the experiment, and in this sample the absorption in the sealed apparatus was two and one-half fold greater than A. On account of the great avidity for oxygen shown by the finely divided coal, it was anticipated that samples E and F which consist of the finest particles, on account of the small amounts of these portions obtained in the sizing, and consequently excessive exposure to the air during preparation, might be fairly saturated before the experiment began. This was the case as indicated by the low speed of the absorption of oxygen after sealing and the comparatively small reduction in the pressure before it began to increase. The fact that not so great a partial vacuum was produced at any time in these as in the fresher samples shows that the rate of the evolution of

TABLE IX.—The oxygen, not including that replaced by carbon dioxide and other evolved gases, absorbed by Batan coal at 30° C.

Time.	Portion A (40 grams in 4,890-liter flask a).			Portion A (100 grams in 4,245-liter flask a).				Portion C (20 grams in 1,894-liter flask a).			Portion C (40 grams in 1,846-liter flask a).			
	Volume b of oxygen absorbed in cubic centimeters per gram of fresh coal.	Per cent by weight of oxygen absorbed referred to the fresh coal.	Pressure in flask.	Volume b of oxygen absorbed in cubic centimeters per gram of fresh coal.	Per cent by weight of oxygen absorbed referred to the fresh coal.	Pressure in flask.	Relative rates of absorption of the 2 samples of portion A.	Volume b of oxygen absorbed in cubic centimeters per gram of fresh coal.	Per cent by weight of oxygen absorbed referred to the fresh coal.	Pressure in flask.	Volume b of oxygen absorbed in cubic centimeters per gram of coal.	Per cent by weight of oxygen absorbed referred to the fresh coal.	Pressure in flask.	Relative rates of absorption of the 2 samples of portion C.
Days.			Mm.			Mm.				Mm.			Mm.	
0	0.00	0.00	754	0.00	0.00	783		0.00	0.00	7.67	0.00	0.00	770	
1	1.00	0.13	747	0.99	0.13	765	1 : 0.99	1.81	0.23	7.47	1.80	0.23	734	1 : 0.99
5	2.15	0.28	739	2.14	0.28	744	1 : 0.99	4.44	0.57	7.18	4.34	0.56	688	1 : 0.98
18	4.30	0.55	724	4.17	0.54	707	1 : 0.97	7.26	0.94	6.87	7.09	0.91	628	1 : 0.98
21	6.17	0.80	711	5.92	0.76	675	1 : 0.96	9.51	1.23	6.61	9.33	1.20	583	1 : 0.98
31	7.75	1.00	700	7.40	0.95	648	1 : 0.95	11.07	1.42	6.45	10.63	1.37	557	1 : 0.96
46	10.05	1.29	684	9.38	1.21	612	1 : 0.93	13.51	1.74	6.18	12.77	1.64	514	1 : 0.95
59	11.77	1.52	672	10.70	1.38	586	1 : 0.91	14.69	1.89	6.05	13.82	1.78	498	1 : 0.94
65	12.77	1.65	665	11.29	1.45	577	1 : 0.88	15.15	1.95	5.99				
125	19.18	2.47	621	15.12	1.95	499	1 : 0.79	20.20	2.60	5.42	17.95	2.31	405	1 : 0.89
c 202	24.28	3.12	583					23.50	3.03	5.05	19.37	2.50	376	1 : 0.88

a Gas volume in flask in cc. = volume of flask in cc. — (weight coal in grams ÷ specific gravity of coal). The specific gravity used in the calculations is 1.3.

b Computed to standard conditions of pressure.

c After this experiment had been in progress about two and one-half months, the various pieces of apparatus used were placed nearer an open window. In all four cases the speed of the absorption of oxygen was greater and in each pair was most accelerated in the apparatus which contained the least amount of coal and which was most exposed to the light. This influence of tropical light will be further investigated. The experiment is still in progress.

carbon dioxide was equal to that of the absorption of oxygen while the latter was still very energetic. The evolution of carbon dioxide depends directly on the previous absorption of oxygen, and therefore the fact that the evolution of carbon dioxide by samples E and F was more rapid than that in any of the others clearly substantiates the assumption as to their previous partial saturation.

The rate of the absorption of oxygen by a given coal varies with its previous exposure to the air. Under the same conditions, it depends upon the size of the grains; it is more rapid in the finer particles, probably approximately proportional to the surface exposed. The absorption of oxygen, not including that replaced by evolved carbon dioxide, was determined in two samples each of portions A and C in an apparatus identical with that shown in fig. 1 and described above, except that flasks of dimensions as indicated were substituted for the 100-cubic-centimeter glass pipette f.

In the larger samples the absorption was so much more rapid that the pressure at which the oxygen was supplied became diminished and the rate of absorption correspondingly reduced. The particles in the samples of the portions were so fine that they packed closely, and particularly in the larger samples the oxygen could not possibly penetrate uniformly to all parts. The relative rate of the absorption of oxygen in the two samples of portions A and of C was never equal to the ratio of their weights. The above experiments also show that the absorption of oxygen is much more rapid during the first few weeks than during the subsequent periods. These points are indicated more clearly when the results of Table IX are represented graphically as shown in fig. 2 in which—

Curve I = Portion A (40 grams in 4.390-liter flask);

Curve II = Portion A (100 grams in 4.245-liter flask);

Curve III = Portion C (20 grams in 1.394-liter flask); and

Curve IV = Portion C (40 grams in 1.546-liter flask).

If coal is stored in air, after a time, the compounds in the coal unsaturated with respect to oxygen become saturated and the avidity of the whole for oxygen becomes much less as shown in Tables VIII and IX. It follows from this that there is much more danger from fire during the early stages of storage, and, because of this fact, when coal has once been stored as a reserve and no serious heating has resulted, it should be left undisturbed and the coal for present consumption taken from the newest piles.
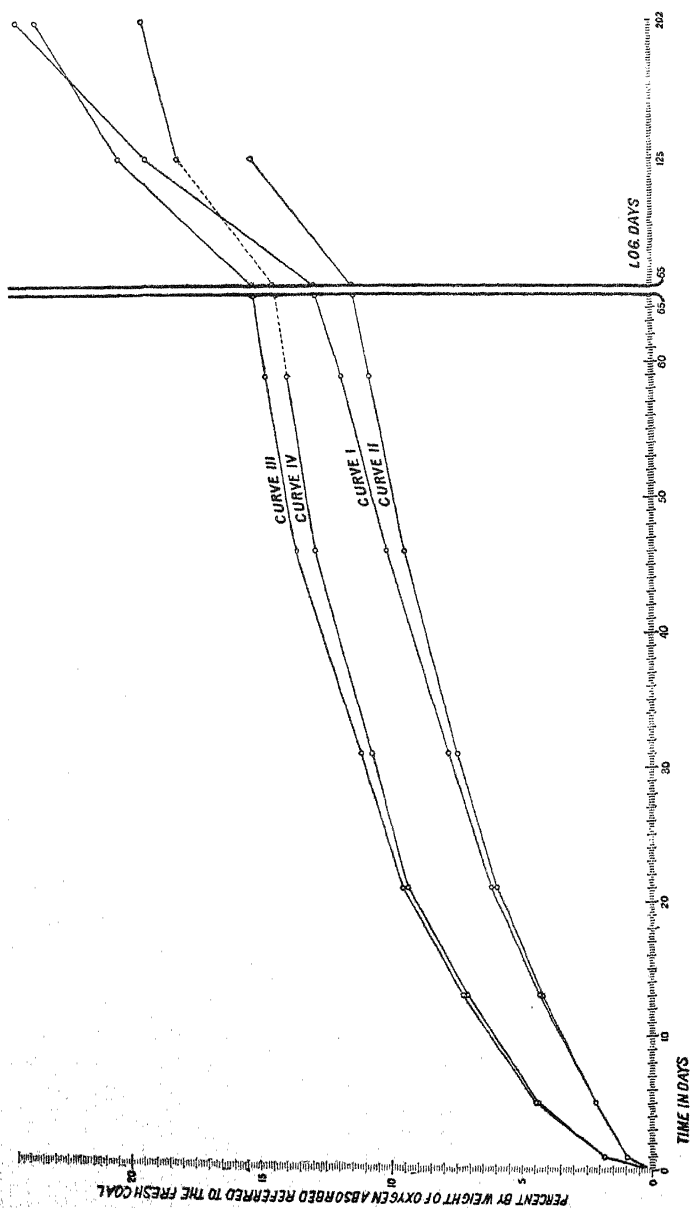
FIG. 2.—Curve representing the oxygen, not including that replaced by carbon dioxide and

The value of the bituminous coal produced in the United States during the calendar years 1907 to 1909 was 1,230,836,887 dollars, an average annual value of 410,278,962 dollars.[6] If bituminous coal suffers an average deterioration of 2 per cent,[7] the annual loss in the United States from deterioration of coal is over 8,000,000 dollars, or 4 per cent as great as the total losses of all property by fire.[8]

There is also a large loss due to spontaneous combustion of coal. Oxidation of combustible matter produces the same amount of heat whether the reaction takes place rapidly or very slowly. If the heat of a slow reaction can not escape, the same increase in temperature will result as when the change takes place rapidly. Every combustible substance has its ignition point, and for it to burn rapidly it must first be heated to the point of ignition. This depends almost entirely on the porosity and the fineness of division, together with the chemical composition. If the substance is in a large compact unit, its ignition is not easily accomplished, but in a very finely divided state and with sufficient oxygen present it may kindle and the combustion be propagated with explosive violence. If the amount of coal in a given heap be small, there will be no perceptible increase in temperature from the heat of the reactions involved, for the heat will all be lost through radiation. But if the escape of heat is prevented, as is done when fine coal is piled in high heaps, and if a supply of oxygen is available, absorption of oxygen with consequent rise in temperature will result. The absorption of oxygen by coal seems to increase rapidly with the temperature, and eventually the kindling point may be reached and visible combustion follow.[9]

[6] *U. S. Geol. Surv. Min. Prod. U. S. Calendar Yrs. 1900–9* (1911), Mar. The average annual production of Pennsylvania anthracite is valued at 157,059,584 dollars.

[7] Parr and Hamilton, *Econom. Geol.* (1907), 2, 703, found that in 20-pound lots of Illinois coal "outdoor exposure results in a loss of heating value varying from 2 to 10 per cent" which substantiates Table IX. *Cf.* also *Engineer* (London) (1903), Oct. 30, and Bement, A., *Chem. Eng.* (1910), 12, 10.

[8] From the data of the National Board of Fire Underwriters, U. S. Dept. Commerce and Labor, Bur. Statistics, *Statis. Abs. U. S.* (1910), 586, the estimated fire losses in the United States for the calendar years 1907 to 1909 aggregate 621,675,709 dollars, an average annual loss of 207,225,236 dollars.

[9] Ordinarily the air furnishes the oxygen for combustion, but it may be supplied by other oxidizing agents. In the latter case oxidation may be so rapid that it causes an explosion. Certain Philippine coals mixed with sodium peroxide at room temperature ignite spontaneously.

In an extremely finely divided state coal will ignite almost as
readily as gas derived from coal. Care must, therefore, be
taken to avoid the ignition of coal dust, as there is no doubt that
many serious fires and explosions are directly attributable to
it and the violence of the latter may have been more severe in
certain cases on account of absorbed oxygen.

The presence of sulphur in the form of iron pyrites in stored
coal has often been thought to be a source of heat and the cause
of spontaneous combustion owing to the reaction between sulphur
and oxygen.[10] It is a fact that with a high content of sulphur
coals often give trouble from heating; on the other hand, coals
containing a small amount of sulphur, not more than 1.5 per
cent, which include practically all of those from the Philippine
Islands, also sometimes heat badly. This can not entirely be
explained by the sulphur present. The amount of sulphur is
far too small to account for the increase in temperature recorded
in many instances even if it were all oxidized, which has never
been shown to be the case. Porter and Ovitz [11] have shown
that there is "a very minor contribution, if any, on the part of
sulphur to spontaneous heating in coal." Bodenstein and Karo,[12]
have shown that for liquid sulphur the velocity of the reaction
with oxygen is proportional to the surface exposed. On the
same principle, the fineness of division of the sulphide in coal
would make its oxidation comparatively rapid and favor spon-
taneous combustion.

The question of the influence of moisture in coal upon its
oxidation has not been sufficiently worked upon to enable us to
decide it. Griswold [13] says that when stored, wet coal should
be spread out to expedite drying, especially when wet with snow
and ice, and Doane [14] says:

The amount of moisture in an air-dried sample of coal is an indication
of its liability to heat, the danger increasing with the percentage of mois-
ture contained. Coal containing over 4.75% after air drying is said to be
dangerous.

The amount of water naturally present in coal is an indication
of the grade and, as already pointed out, the kind of coal is a
factor upon which oxidation partly depends. Aside from this,
it is probable that the amount of moisture has little significance.

[10] Cf. Parr and Kressman, Journ. Ind. & Eng. Chem. (1911), 3, 151.

[11] Journ. Ind. & Eng. Chem. (1912), 4, 7.

[12] Ztschr. f. phys. Chem. (1910), 75, 47.

[13] Eng. News (1904), 51, May 5.

[14] Ibid. (1904), 52, 141.

The action of sunlight on coal not only increases its temperature directly, but also catalytically by accelerating the absorption of oxygen, and thus in two ways it increases deterioration and the danger from spontaneous combustion.

A coal which illustrates these points is that now being mined on the eastern end of the Island of Batan.[15] On exposure to the sun and air it alters rapidly, loses its luster, and falls into powder. It slakes in shipping, unless it is kept from the sun and wind while in transit. Spontaneous combustion has several times occurred in this coal, but the particulars are not available, except in the more recent cases. The Civil Government of the Philippine Islands used some coal from the Batan mine during 1911 and had trouble with 9,000 tons of the same coal in piles about 5 meters high placed on the ground under a roof. The piles were ventilated with alternate tiers of horizontal air passages, about 6 meters apart and at right angles to each other. In this case there was no actual flame, but all of the timber used to make the ventilators was badly charred.

In coal heating in bunkers, even though the temperature be only moderately raised, there is an increased escape of volatile combustible matter and consequent loss of fuel value. Evidently the danger from spontaneous combustion of coal may be reduced by assisting in every possible way the dissipation of heat through radiation by having the coal sufficiently close to air-cooled surfaces,[16] but any system which brings the air freely into contact with the coal should be avoided. Ventilation of this sort may mean danger of fire, because it is very difficult to provide sufficient radiation to remove the heat as fast as it is formed. Storage piles should be protected from the sun and every other external source of heat.

Any method which protects the coal from the air will preserve it. This can unquestionably be done by submergence in water, but this necessitates firing wet coal.[17] Firing of wet coal may be avoided by dry storage in carbon dioxide or other inert gas. I believe there will be little danger from fire in storage of this sort, for the air supply is cut off. Deterioration

[15] This coal is a poorer grade than that from the western end of the island.

[16] The coal should be stored in bunkers which have surfaces large in proportion to the bulk, or air might be circulated through the heaps in iron pipes in such a way that it does not come in contact with the coal.

[17] Parr and Hamilton, *Econom. Geol.* (1907), 2, 703, "Submerged coal does not lose appreciably in heat value." See also the bibliography at the end of this paper.

probably may be as effectually avoided by the use of bunkers, with tight floors and sides and fairly close-fitting covers, filled with carbon dioxide as by storage under water. The following experiments show the effectiveness in preventing deterioration by the exclusion of air through inert gases. Two 250-gram samples of each coal, one in nitrogen and the other in carbon dioxide, were stored for about nine months in 10-liter bottles at about 30° C. in an ordinary room lighted by diffused sunlight.

TABLE X.—*Analyses and calorific values of Philippine coals stored in nitrogen and in carbon dioxide.*

Coal No.	Original sample.					After storage in nitrogen.			After storage in carbon dioxide.		
	Moisture.	Volatile combustible matter.[a]	Fixed carbon.[b]	Ash.	Calories.[c]	Moisture.	Ash.	Calories.	Moisture.	Ash.	Calories.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*		*Per ct.*	*Per ct.*		*Per ct.*	*Per ct.*	
1	5.90	46.30	40.08	7.72	6,159	5.48	7.66	6,227	5.56	6.97	6,249
2	8.61	40.67	46.55	4.17	6,012	8.46	4.05	6,050	7.68	4.91	6,057
3	11.55	37.43	46.95	4.07	6,066	10.39	3.81	6,199	10.86	3.88	6,161

[a] After the method of Cox, *This Journal,* Sec. A (1907), 2, 41.

[b] Each analysis shows somewhat less ash than the ordinary coal from the same source because of the way in which the samples were prepared.

[c] Average of three closely agreeing, independent determinations.

The above results calculated to the uniform basis of pure coal show that there was no deterioration on storage.

TABLE XI.—*The calorific value of coals stored in nitrogen and in carbon dioxide.*

Coal No.	Calorific value of the pure coal.[a]			Variation from original sample in calories.	
	Original sample.	After storage in nitrogen.	After storage in carbon dioxide.	Stored in nitrogen.	Stored in carbon dioxide.
1	7,130	7,168	7,144	+38	+14
2	6,893	6,914	6,929	+21	+36
3	7,189	7,225	7,226	+36	+37

[a] An interesting comparison is that of Table XI with Table II from which it will be seen that the coal stored in air has a calorific value about 2 per cent less than that stored in either of the above inert gases.

Table XI shows an increase in calorific value during storage. I can not explain this, but it is probable that it is due to the evolution of carbon dioxide rather than to experimental error. That such change does take place in a coal which has absorbed

oxygen subsequent to the removal of the oxygen supply is shown by the following facts.

An analysis of the residual gas above coal 1 stored in nitrogen gave the following results:

Constituent.	Per cent.
Carbon dioxide	0.6
Oxygen	0.0
Nitrogen	99.4

To demonstrate beyond question that the small amount of carbon dioxide did not result from a slight leakage of air through the rubber stopper and subsequent oxidation of coal, proportionately larger portions of coals 1 and 2 were sealed off in an atmosphere of nitrogen in flasks. After one year they were opened, and in each case the pressure was found to be increased by a small amount and the gases had the following composition:

Constituent.	From flask containing coal No. 1.	From flask containing coal No. 2.
	Per cent.	Per cent.
Carbon dioxide	4.0	5.0
Oxygen	0.0	0.0
Nitrogen	96.0	95.0

The same sort of deterioration as I have just described takes place along the outcrop of coal beds and is limited only by the nature of the coal and the penetration of the air. The latter is not very great in well-watered regions like the Philippine Islands where the ground-water table is high, but in arid regions it is natural to suppose that the air may penetrate and deterioration take place proportionately in greater depths. However, recent work has shown that deterioration does not always extend to the ground-water level or even to a considerable portion of the distance.

This paper gives results which are by no means complete, and leaves several points unsettled and much to be accomplished. Only the preliminary investigation has been carried on, but with the information and experience derived from it the author hopes more effectively to continue the work.

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ILLUSTRATIONS.

SAND-LIME BRICK AND ARTIFICIAL SAND STONES IN THE PHILIPPINES.

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INTRODUCTION.

Sand and limestone, although the most common and familiar and perhaps the least appreciated of mineral resources, constitute an asset of immense importance to any country. Limestone of excellent quality is abundant throughout the Philippine Islands [1] and guarantees to this Archipelago important industries, among which the manufacture of artificial stone and brick from sand and lime is certain to become exceedingly important.

In the Philippines, the varieties of stone which are known to be good for building and construction purposes are not very numerous, and it is unfortunate that with the exception of a few deposits of volcanic tuff ("adobe" stone), those which exist are not conveniently located for use. In the past, most of the permanent buildings were constructed of volcanic tuff, and its low and uncertain strength [2] made very massive construction work necessary. Moreover, as the stones have a dirty color and are only roughly shaped by hand into rectangular blocks 18 by 18 by 50 centimeters in size, they give structures a very unclean, irregular, and aged appearance.

A superior volcanic tuff is quarried at Meycauayan, Bulacan, about 10 kilometers from Manila. Six-inch cubes of this material gave a crushing strength of 1,047 pounds per square inch (73.6 kilograms per square centimeter). However, the data recorded in Table I show that most of the volcanic tuff extensively

[1] Adams, G. I., *This Journal, Sec. A* (1910), 5, 57–117. Smith, W. D., *ibid.* (1906), 1, 1043–1061; *Sec. A* (1910), 5, 307–363.

[2] Cox, Alvin J., *This Journal, Sec. A* (1908), 3, 191.

used throughout the Island of Luzon is a very poor building material.

TABLE I.—*Compression strength of 6-inch cubes of volcanic tuff.*

Quarry.	Date mined.	Weight per cubic meter (average).	Total strength in pounds.		Average strength in pounds per square inch.	
			First crack.	Ultimate.	First crack.	Ultimate.
		Kilos.				
Binangonan	Apr. 17, 1876	1,540	ª4,300 6,500 5,650 16,200	ª6,500 12,500 12,800 16,300	263	385
Cauit	July 14, 1879	1,480	5,300 9,700 3,400 6,500	6,550 9,900 4,800 6,600	173	193
Unknown	Sept. 8, 1880	1,456	8,550 4,100 8,000 5,900	8,850 6,675 8,550 6,350	184	212
Bañadero	July 1, 1882	1,520	4,300 3,500 5,600 9,400	7,100 7,000 8,000 11,040	159	230
Do	Jan. 17, 1912	1,560	2,300 5,250 . 6,700	4,250 5,400 3,700 7,800	123	147
Binangonan	do	1,665	10,000 8,500 7,200 14,000	16,425 16,950 16,650 17,100	276	467
Cauit	do	1,665	8,000 5,100 6,900	6,525 8,760 7,825 7,250	185	211

ª Corners of cube broken off.

Recently, important structures have been built almost exclusively of reinforced concrete, and concrete blocks have been used for small buildings. The high cost of cement and good

aggregate makes such work expensive, but in spite of this and the great need of a cheap and durable building stone the sand-lime brick industry has not been introduced into these Islands in any form.

The latest and best methods for the manufacture of artificial sandstone place the process midway between a quicklime and a cement industry, and important technical considerations are involved. The most efficient methods of quarrying and burning limestone, of slaking lime, of mining and grinding the raw materials, and of molding and hardening the products have not yet been determined. Also, the effect of impurities such as clay, feldspar, and dehydrated kaolin have not been thoroughly investigated. However, sufficient information is available to insure the commercial value and feasibility of this industry in the Philippines if it is carefully and conservatively managed after a proper selection of a factory site, raw materials, process of manufacture, and machinery. On the other hand, if the cost of production includes large items for "promotion," "secret formulas," etc., the stability and success of the enterprise are questionable.

This laboratory is carrying on a thorough investigation to ascertain the suitability and relative efficiency of available raw materials for the manufacture of sand-lime bricks and to study some of the most important technical considerations involved. This work is far from complete, but owing to numerous requests for data on the subject the publication of these preliminary notes seems advisable. The information herein contained is not intended to cover all the possibilities and processes of the industry nor the technical conditions involved. A discussion of these points may be found elsewhere.[3]

CARBONATE BINDER.

Previous to 1880 lime-mortar bricks were manufactured simply by molding a stiff mixture of sand and slaked lime by hand and then exposing it to the sun and air. The hardening process involved depends primarily upon the conversion of calcium hydroxide into calcium carbonate. It is slow and comparatively expensive, as several months' time and a very large percentage

[3] Peppel, S. V., *Bull. Geol. Surv. Ohio* (1906), 5. Essais sur le Silico Calcaire, by E. Leduc, current numbers of *Cem. & Eng. News,* and the *Tonind.-Ztg.*

of lime are required for suitable results.[4] On the other hand, the durability of lime mortar is unquestionable. Lime-mortar brick buildings in Germany, England, and America which can be readily traced considerably over fifty years are still in excellent condition. More rapid and efficient methods of accomplishing the same results have practically abolished this process of manufacture, but in some parts of the Philippine Islands the conditions are such that the old process might be employed with success. In Masbate, Surigao, Cebu, Benguet, and other provinces there are places where an abundance of firewood, limestone or seashells, and sand are available; and in such places the ordinary laborer could build his own lime-kiln and wooden molds and manufacture mortar brick without capital.

When it was discovered that mortar brick hardened equally well in an atmosphere of carbon dioxide or waste furnace gases, the factor of time was largely eliminated. The process was further improved by molding the bricks under great pressure and also by hardening with carbon dioxide (CO_2) under pressure. We do not believe that any of these methods will ever become of commercial importance, because the conversion of lime into calcium carbonate is confined more or less to exposed surfaces of the mortar as well as to the individual particles, and this precludes the possibility of great strength and uniform and reliable results.

CALCIUM HYDROSILICATE BINDER.

In 1880 the researches of Michaelis Sr. of Berlin resulted in the process of making sand-lime brick in which the sand particles are bound together by calcium hydrosilicate. The principle involved is very simple. Sand or finely crushed stone is thoroughly mixed with about 10 per cent of slaked lime and the moist mixture molded under great pressure into any desired shape. When molded, the bricks are piled on trucks and wheeled into a large steel chamber where they are subjected to the action of live steam under pressure. The time required for proper steaming depends upon the steam pressure employed, but eight hours at 130 pounds per square inch (9.13 kilograms per square centi-

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[4] The crushing strength of lime mortar is only about 150 to 300 pounds per square inch (10.5 to 21.1 kilograms per square centimeter) and this maximum strength is attained in about one and one-half years.

meter) gives very satisfactory results. After the steam treatment, the bricks are ready for immediate use.

The best commercial practise results in a very desirable product. The strength is as high as, and more uniform than, a good quality of stone, and it increases with age; the absorption of moisture is less than that of any other except vitrified brick, and it is remarkably little affected by heat. The best commercial practise in America produces a sand-lime brick with compressive and tensile strengths ranging from 4,000 to 6,500 and from 300 to 370 pounds per square inch (280 to 460 and from 21 to 26 kilograms per square centimeter) respectively. These figures can be increased to 8,500 for compression and 550 for tension, but a compressive strength of 4,000 and a tensile strength of 300 pounds per square inch are sufficient for all ordinary brick construction work.

The sand-lime brick industry has reached its highest state of commercial success in Germany where over 300 factories have been in successful operation for many years. Practically no face bricks are manufactured, but the largest factory, the Berliner-Kalksandsteinwerke near Berlin, operates continuously and produces 440,000 bricks daily. The success of the industry in Germany is due largely to the control of an association of sand-lime brick manufacturers which, since 1903, put its members under obligation to manufacture brick having a crushing strength of not less than 2,000 pounds per square inch (140 kilograms per square centimeter). The sand-lime brick industry has not gained much prominence in the British Isles, for the reasons that in England there are immense deposits of first-class clay which enable clay bricks to be produced and sold at a very low price, while in Scotland good stone quarries are plentiful and building stone is a cheap commodity. The industry was introduced into the United States in 1901, but did not make much progress until 1903 when 16 plants reported products valued at 155,040 dollars. During the next four years the industry grew rapidly, 94 plants reporting 1,225,679 dollars' worth of products in 1907. Since then it has declined, and in 1911 there were but 66 firms, and the total value of their production dropped to 879,664 dollars.[5] A careful investigation of the cause of this decline has led us to believe that it was due to the marketing of an improperly prepared product and to the fraudulent practises of

[5] *U. S. Geol. Surv. Press Bull.* (1912), **53**, 1.

promoters and manufacturers. Such practises serve to destroy the confidence of the financier, architect, and general public, and their object lesson is one which must be heeded. A competition for cheapness and not for quality is the most frequent and certain cause of failure.

Michaelis permitted the letters patent on this process of hardening by superheated steam to lapse without commercial application, and therefore it is public property. No secret formulas or chemicals are necessary, and, if the available raw materials are satisfactory, manufacturers are willing to enter into contract to furnish working drawings and blue prints for the necessary foundations and buildings, equip and install the machinery, and put the whole plant in proper operation. There are a few patents concerning the economy of manufacture which have more or less merit, but recently an all-American system with no patents has been introduced.

MIXED CARBONATE AND SILICATE BINDER.

A combination of the two hardening processes just described provides for the introduction of carbon dioxide from the lime kilns and steam into closed iron chambers. The binding material formed at atmospheric pressure is mainly calcium carbonate. The amount of calcium silicate formed increases with the steam pressure, while that of the carbonate decreases.

Peppel [6] believes that sand bricks with a silicate bond are the only ones which will ever take any important place in the world's markets, but an inspection of the works and products of the British Stone and Marble Co., Ltd., Ponders End, Middlesex, England, gives an entirely different impression. This company uses and claims to own a process whereby the débris of any suitable building stone is first reduced by mechanical disintegration to a granular state and then built up again into stone practically indistinguishable from the quarried product. As its trade name indicates, it is "reconstructed stone." The characteristic features of the natural product are produced with accuracy while the defects are eliminated. The process consists in disintegrating quarry débris without destroying the form of the original component grains, mixing the resultant grit with a definite proportion of lime calcined in closed retorts, slaking the mixture thoroughly, and, after the addition of considerable water, consolidating under great pressure into blocks of any desirable size

Loc. cit.

and shape. These blocks are of the consistency of soft chalk when they leave the press, and since they are homogeneous they can be easily and rapidly shaped with saws and cutting tools. After being cut or carved to any required design, the material is dried at a temperature of 40° to 50° and placed in steel tanks from which the air is exhausted; carbon dioxide previously expelled from dolomite is then admitted by successive stages together with some steam until the carbonation of the hydrate of lime is complete. The stone is then ready for sale, unless sanding or gritting is desired.

Any kind of sedimentary rock, whether granular or metamorphic, can be reconstructed by this process which converts both hard and soft, perfect and imperfect, natural products into uniformly hard and durable stone of superior quality and appearance. Quarry débris is preferable to ordinary rock only because of the difference in the state of pulverization. It would be too expensive to crush hard rock solely for this purpose, but there are many soft stones in the Philippines which crush so easily that the cost would not be prohibitive.

Information regarding the durability of reconstructed stone is not available, but the bonding is unquestionably uniform and complete throughout the mass, which indicates that it should weather with uniformity and prove durable even under very severe atmospheric conditions. The resistance to crushing stress of 3-inch cubes of reconstructed stones is given in Table II.

TABLE II.—*Crushing strength of reconstructed Bath stone.*[a]

Test No.	Total strength in pounds.		Average strength in pounds per square inch.		Average strength in tons per square foot.	
	Slightly cracked.	Crushed.	Slightly cracked.	Crushed.	Slightly cracked.	Crushed.
2424	109,600	127,700	11,264	13,124	724.4	844.0
2422	96,700	120,100	9,938	12,343	639.1	793.8
2623	84,000	98,200	8,571	10,020	551.2	644.4
-------	96,765	115,333	9,924	11,829	638.2	760.7

[a] Tests made by David Kirkaldy and Sons, London, England, and published in the manufacturers' pamphlet, "About Reconstructed Building Stones and Marble."

The poor fire-resisting properties of this stone are detrimental to its efficiency as a constructive material. The binder is principally calcium carbonate, and a red heat will cause disintegration.

USES FOR SAND BRICK AND ARTIFICIAL STONE.

Good sand-lime bricks are sanitary, their hygroscopic properties are very slight (about 1.5 per cent in air), they absorb very little water when wet (6 to 10 per cent), do not effloresce, and in every way apparently meet the demands of tropical climatic conditions as a desirable structural material.

We have considered only the application of these processes to the manufacture of ordinary building stone. Fortunately there are other uses to which either the reconstructed stone or the sand-lime process can be applied; namely, the manufacture of building blocks, sills, caps, fence posts, slabs, tiles, wall-copings, templates, jambs, lintels, steps, landings, curbstones, pipes, sidewalk slabs, and ornamental work such as elaborate moldings, monuments, flower pots, posts, vases, statuary, garden seats, and artificial marble. Plate I shows a small segment of a reinforced, reconstructed-stone beam designed to support glass plates on the roofs of hothouses. The photograph shows the smooth hard surfaces and clean edges obtainable, and suggests a wide range of application for artificial sandstone products such as are shown in Plate II. The various articles may be manufactured in trade sizes and patterns by tamping portions of the raw mixture into special molds and then hardening in the usual manner; or the material can be pressed into blocks, and, while still soft, cut by hand or machine into almost any design. Frequently the profits of a sand-brick plant can be augmented by manufacturing such articles, and the expense for the necessary additional equipment is comparatively small.

The manufacturer of sand brick or artificial stone must depend upon large and fairly regular sales for profitable returns. A factory with a capacity and market below 15,000 bricks per day would probably not be a very good investment. It will require several years to create a demand in the Philippines large enough to keep a factory of greater capacity in constant operation. On the other hand, there is a demand for such articles as fence posts, tiles, steps, sidewalk slabs, pipes, and ornamental work, and a plant equipped to manufacture these as well as the ordinary building stone has an opportunity successfully to establish a good and growing business.

The usual, continuous horizontal joints of brick walls are a source of weakness. This is especially undesirable in countries subjected to earthquake shocks, and should be overcome by special

forms of brick which, when properly laid, result in broken and bonded horizontal as well as vertical joints,[7] or by interlocking or reinforcible building blocks, similar to concrete blocks now in use, both of which can be easily manufactured.

RAW MATERIALS.

Sand brick or reconstructed stone can be manufactured on a commercial basis with either calcium carbonate or calcium hydrosilicate as the binding material. The former has for its advantage a minimum fuel consumption, while the latter withstands best the effects of fire and, in all probability, atmospheric and chemical influences. The calcium carbonate process is not dependent upon the chemical composition of a sand or stone, but silica in a suitable chemical or physical condition is essential to the steaming process. With the exception of these differences, further consideration can be limited to the calcium hydrosilicate, the so-called sand-lime brick process.

Siliceous material.—Generally speaking, common siliceous sand is the most desirable and the cheapest source of silica for the sand-lime brick industry. A fairly good sand-lime brick can be obtained with almost any sand, but economy in manufacture limits the physical and chemical properties rather sharply. A comparatively pure and fine sand is essential to a cheap and durable product, and silica which is capable of combining with the lime must be present in quantity. Sand grains too large to pass a sieve having 8 meshes to the centimeter (20 meshes to the inch) are undesirable, and particles sufficiently fine and numerous to enable sufficient silica to combine with the calcium oxide are necessary.[8] In order to produce a dense brick, there should be a good gradation of sizes and a low percentage of voids. Very few natural sands have this desirable granularimetric composition, and the influence of fineness upon the quality of the brick is so great that usually it is advisable to resort to screening and grinding or what is known as the division method. Screens are employed to remove the large particles, and granularimetric gradation is accomplished by grinding part of the sand and then remixing this pulverized product with the whole. The lime is ground with the sand in order to secure as thorough a mixture as possible.

[7] Strale, A. N. H., Pat. No. 1,021,851, April 2, 1912.

[8] Gasenapp, M., *Tonind.-Ztg.* (1901), 762.

Quarry débris, soft stone, and volcanic tuff are often suitable sources of silica and in many instances are capable of being crushed into desirable sand at no greater cost than that required for the installation of the division method. Siliceous sands, soft sandstone, and volcanic tuff are plentifully distributed throughout the Philippine Islands.

Richly colored siliceous materials naturally give bricks of a similar color, but otherwise a pleasing white to gray is obtained which is more or less spotted according to the color, quantity, and shape of the coarse grains. The color is permanent, unless oxidizable mineral pigments such as iron are present.

Lime.—In ordinary lime mortar, magnesia is not considered detrimental, but it can not be substituted for calcium oxide in the sand-lime brick industry on account of its slow slaking properties. Other impurities in the limestone, such as sand, clay, and iron oxide, should also be avoided. They tend to produce slow slaking, fluxed and overburned lime,[9] as well as to decrease the efficiency by dilution. On the other hand, a comparatively pure calcite limestone gives the best results, and can be burned and slaked with the least expense and difficulty. It is absolutely necessary that the free lime be thoroughly hydrated before the bricks are molded; otherwise, the expansion due to subsequent hydration is very apt to cause the bricks to swell or crack and split.

In the Philippines, the most generally distributed calcareous material is a hard limestone of Miocene age which is usually associated with shales and sandstones. It occurs abundantly on nearly every island of the Archipelago and is uniformly remarkably pure.[10] Its fitness for the sand-lime brick industry is demonstrated by the analyses given in Table III.

[9] The evil effect of free lime and magnesia in sand-lime brick is in all respects similar to their effect in indurated Portland cement, and the slaking properties of free lime under all conditions of burning, grinding, and seasoning are important considerations. *Cf.* Reibling W. C. and Reyes, F. D., *This Journal, Sec. A* (1910), 5, 117–142; (1911), 6, 207–252; (1912), 7, 135–191.

[10] Cox, A. J., *This Journal, Sec. A* (1909), 4, 211; Pratt, W. E., *Min. Resources P. I. for 1910, Bur. Sci., Div. Min.* (1911), 61.

TABLE III.—*Analysis of Philippine limestones.*

Sample No.	Source	Classification.a	Silica (SiO₂).	Alumina (Al₂O₃).	Iron oxide (Fe₂O₃).	Lime (CaO).	Magnesia (MgO).	Alkalies (Na₂O + K₂O).	Loss on ignition (mostly carbon dioxide).
1	Mount Licos near Camansi coal mine.	Miocene limestone.	0.36	0.18		55.62	0.00	--------	43.93
2	Marble, Romblon, Capiz.	-----do ---------	0.10	0.17		55.23	0.45	--------	43.50
3	Batan Island, Albay.	-----do ---------	0.97	0.56	0.36	53.86	0.19	---- ----	43.13
4	Cebu, Cebu -----	Coralline limestone (Pliocene).	1.31	3.90		52.01	0.63	--------	--------
5	Danao, Cebu----	-----do ---------	2.61	2.23		52.85	0.88	--------	--------
6	Guimaras Island.	-----do ---------	6.28	4.33		45.76	2.70	--------	--------
7b	Naga, Cebu-----	Coralline marl (Pliocene).	11.12	4.28		45.65		--------	--------
8	-----do ---------	-----do ---------	14.10	5.77		43.27		--------	--------
9	-----do ---------	-----do ---------	11.57	4.62		46.25		--------	--------
10	-----do ---------	-----do ---------	12.68	5.75		43.36		--------	--------
11	-----do ---------	-----do ---------	9.43	4.02		47.53		--------	--------
12	-----do ---------	-----do ---------	10.28	0.63	3.28	45.96		--------	--------
13	-----do ---------	-----do ---------	8.37	0.22	3.25	49.84	1.02	--------	--------
14	-----do ---------	-----do ---------	11.99	0.57	2.90	45.69		--------	--------
15	Argao, Cebu-----	Bedded marl or chalk (Pliocene).	8.93	6.45		44.35	2.70	--------	--------
16	Near Camansi --	Argillaceous limestone (Miocene).	29.00	11.38	5.35	26.25	0.65	1.98	23.00
17	-----do ---------	-----do ---------	24.02	7.49	2.00	33.88	2.12	--------	28.25

a Made by W. E. Pratt.

b Analysis typical of a series of best hole samples representing a thickness of from about 15 to 30 meters over an area of about 15 hectares.

In general, the physical condition of Philippine limestones is also very satisfactory. Their hardness, while sufficient to insure solidity during the burning process, is not great enough to

prevent easy quarrying. The burning and slaking of lime and its incorporation into sand are apparently simple operations; however, in reality, they involve complicated financial and technical considerations which are almost entirely ignored in local practises. The Filipinos manufacture on a small scale a very poor lime from seashells. They burn with wood or sawdust, and the analysis given in Table IV is typical of the poor quality produced.

TABLE IV.—*Analysis of burned shell taken from a Gagalañgin lime kiln near Manila.*

Constituent.	Per cent.
Total calcium oxide (CaO)	61.4
Carbon dioxide (CO_2)	14.5
Clay, sand, etc.	24.1
Total	100.0
Calcium carbonate [a] ($CaCO_3$)	32.9
Calcium oxide in calcium carbonate (CaO as $CaCO_3$)	18.4
Total impurities ($CaCO_3$ + sand, clay, etc.)	57.0
Available lime [a] (CaO)	43.0

[a] Calculated.

Lime in small quantities is also manufactured from lime rock, but it usually contains at least 40 per cent of underburned material. The only first-class lime which can be purchased in the local markets is that which has been imported from Hongkong or other foreign ports.[11] The prospective manufacturer should burn his own lime, and supply as well the demand for this material throughout the Islands.

The location of the raw materials with respect to the market and the transportation rates are considerations of great importance. The sand or crushed stone constitutes about nine-tenths of the finished product, and, taking into account only the cost of transportation, the relative importance of the location of the limestone, sand, and market, with respect to the plant may be represented by the figures 1, 9, and 10 respectively. The cost of transportation will be reduced to the lowest figure if the location of the distributing market and silica and limestone deposits coincide. Otherwise, the location of the sand with respect to the market is much more important than that of the limestone. The plant should be located as near the distributing center as is practicable.

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[11] Recent imports of slaked lime from Hongkong showed a purity of about 85 per cent.

PROCESS OF MANUFACTURE.

While there are several processes and machines, there are but two distinct systems for controlling the raw mix; namely, the "silo system" and the "pre-hydrating system."

Silo system.—The lime is pulverized, mixed with sand, moistened, and placed in a bin where it is allowed to remain a sufficient time for the lime thoroughly to hydrate or slake. According to E. Leduc and Ch. de la Roche,[12] "stale or partly carbonated limes account for a great number of failures in the manufacture of sand-lime brick," where the silo system is used. Their results (Table V) show considerably less strength when the lime had been exposed to air for four days, and they also obtained less strength when the quicklime had been less finely subdivided or less thoroughly mixed.

TABLE V.—*Effects of air slaking and screening the lime and negligent mixing (bricks steamed for six hours at 120 pounds pressure).*

Lime in the mixture.	Sand in the mixture.	Initial compression of the mixture.	Average resistance to pressure in pounds per square inch.			
			Mix No. 1.	Mix No. 2.	Mix No. 3.	Mix No. 4.
			Results obtained with pure, nonaërated, screened lime, and good mixing.	Same as No. 1 except that the mixing was less thorough.	Same as No. 1 except that the lime was partly carbonated by a 4-day exposure to the air.	Same as No. 1 except that the lime was not sieved.
Per cent.	*Per cent.*	*Pounds.*				
8	92	3,750	1,680	1,340	1,088	1,340
10	90	3,750	2,025	1,470	1,515	1,530
12	88	3,750	2,005	1,480	1,575	1,845
8	92	7,500	2,145	1,750	1,546	1,742
10	90	7,500	2,456	1,865	1,772	1,818
12	88	7,500	2,615	2,130	1,988	2,080

The pre-hydrating system.—This process consists in the hydration of the lime in the hardening cylinders before it is mixed with the sand. This method of slaking utilizes the heat of hydration and insures the use of lime which will not undergo further slaking during the steaming process; but according to P. L. Simson,[13] pre-hydrating systems are gradually being elimi-

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[12] *Cem. & Eng. News* (1911), 23, 231.
[13] *Ibid.* (1912), 24, 164.

nated from up-to-date practise in Germany, where hydrating the lime with all the sand in silos or slaking drums is advocated by the experts.

The advisability of slaking some limes with steam under pressure before mixing with the sand is illustrated by fig. 1, Plate III, and fig. 2, Plate V. In both instances the same raw meal was employed, but the former was made according to the silo system and the latter by pre-hydration. In this instance the pre-hydration was accomplished simply by treating the quicklime with a slight excess of water in a closed air-tight retort. The heat of hydration was sufficient to generate and maintain steam under pressure for several hours.

The degree of compactness affects some mixtures more than others, but in all instances a molding pressure of from 10,000 to 15,000 pounds per square inch (700 to 1,050 kilograms per square centimeter) is required for maximum strength. However, the efficiency of either the raw materials or the commercial value of the finished product does not depend solely on the strength of the brick obtained, but also upon appearance, density, absorption, fire-resistant properties, etc. Furthermore, these are all subject more or less to the conditions of manufacture, such as granularimetric composition, thoroughness of mixing, and molding pressure. A certain coarseness of grain and porosity often improves the fire-resistant properties of a brick, but this is gained only at a sacrifice of strength and density. A practically unlimited range of colors can be produced by the use of artificial coloring matter. The ordinary cheap mineral pigments give fairly satisfactory result, but Glasenapp [14] advocates the staining of sand-lime brick by a new method in which the colors are formed by the reaction of calcium hydroxide with salts of various metals. If polished surfaces are desired, coarse grains of hard durable stone are essential. Marble effects and staining are usually accomplished at the expense of the strength.

Fuel.—Almost any commercial fuel is capable of meeting the demands of this industry. The highest temperature required is for burning the limestone, and as this should be from about 950° to 1,050°, firewood, coal, crude petroleum, natural gas, coke, reduced oil or petroleum residuum, water and producer gases, and even lignites and peat compressed into briquettes have been successfully employed. A long flame of low intensity tends to produce a uniform distribution of heat and to prevent over-

[14] *Tonind.-Ztg.* (1899), 1421.

burning, while the presence of moisture or steam lowers the temperature at which limestone is decarbonated. Wood is the fuel which is best suited technically for burning limestone. Coal, to give the best results, should be high in volatile constituents, hydrogen, and calorific value, and low in fixed carbon, sulphur, and ash.

LABORATORY METHODS.

In testing the siliceous materials, the following general method of making sand-lime brick was used. When necessary, the sand or crushed stone was dried in the air and ground to almost its final degree of pulverization. Then 10 per cent by weight of dry, pulverized, hydrated Montalban lime was ground with part of the siliceous material, and the whole thoroughly mixed before and after the addition of water. The mixture was then molded into bricks under pressure as indicated in the tables, and finally the bricks were subjected to the action of live steam at a pressure of 125 pounds per square inch (8.79 kilograms per square centimeter) for five and one-half to eight hours, as specified.

The first experiments were made to ascertain only the general adaptability of the available raw materials, and no attempt was made to secure better conditions and results than would have been obtained had the material been subjected to an ordinary commercial process for the manufacture of common brick. In fact, it was our desire to make the test a severe one, and for this reason the bricks were molded at the low pressure of 4,600 pounds per square inch or less, steamed only five and one-half hours, and no attempt was made to secure the greatest density or most desirable fineness. After this, the materials were tested under more favorable conditions in order to ascertain their fitness for the manufacture of face brick, tiles, ornamental stonework, fire brick, etc. We have not had sufficient time to make a detailed study of each material such as would enable us to subject each to ideal conditions of manufacture, and the results obtained and recorded throughout this paper can be, and in many instances have been, improved by more thorough mixing, better granularimetric composition, and a higher molding pressure.

P. L. Simson [15] has pointed out that the ordinary American method of testing the strength of bricks on their largest flat surface gives about 30 per cent higher results than the German method of dividing the brick in two and placing one-half above

[15] *Cem. & Eng. News* (1912), 24, 160.

the other. Our bricks were either tested in cubical form or standing on their smallest flat surface, and consequently the results represent a minimum strength. The strength obtained is considered as very satisfactory, and even the lowest is regarded as sufficient for ordinary local construction work, as a 1:2:4 concrete mixture as ordinarily prepared from Philippine aggregate will crush under a pressure seldom exceeding 2,000 pounds per square inch (140 kilograms per square centimeter). On the other hand, the poorest result was much stronger than the best volcanic tuff. However, it is evident that a high molding pressure is essential if a strength above 2,000 pounds is required.

A thorough investigation of the efficiency of the raw materials with respect to the fire-resistant properties of the sand-lime bricks has not yet been accomplished. Certain samples of the sand-lime bricks described in the following pages were heated for thirty minutes in a muffle furnace at about 1,100° and then quenched in water. Plate VIII shows five instances where the bricks remained perfectly sound after such treatment.

RAW MATERIALS IN THE VICINITY OF MANILA.

The high cost of land transportation throughout the Philippine Islands makes the location of the factory with respect to the market and raw materials a consideration of more than usual importance. Eventually, sand-lime brick factories should be installed at all of the principal commercial centers of the Archipelago where suitable raw materials are available in order to reduce the necessary transportation to a minimum. For several years to come the demand in the Philippines will probably not be great enough to support more than one, or possibly two, sand-lime brick plants; and since Manila appears to be the most desirable location for the first plant, the near-by raw materials have been given primary consideration.

Lime.—The most available and important calcareous raw materials in the vicinity of Manila are two exposures of Miocene limestone, one near Montalban, about 30 kilometers from Manila, on a line of the Manila Railroad Company and the other in a semi-mountainous country about 7 kilometers north of Binangonan, Rizal Province, and about 20 kilometers from Manila. There is communication between Binangonan and Manila by means of launches and scows via the Pasig River and Laguna de Bay. The limestones in both places are hard and crystalline, and the deposits are uniform in chemical composition. The analyses given in Table VI show that they are almost pure calcite.
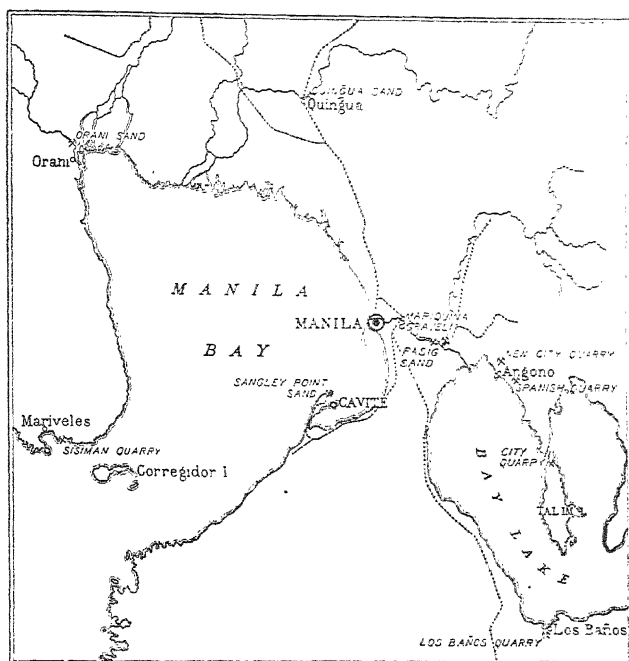
Fig. 1.—The vicinity of Manila (1 millimeter equals 1 kilometer).

TABLE VI.—*Ultimate chemical composition of Binangonan and Montalban limestones.*

Constituent.	Limestone from Binangonan.	Limestone from Montalban.[a]
	Per cent.	*Per cent.*
Water at 110° C	0.16	0.25
Silica (SiO_2)	1.12	0.94
Iron and aluminum oxides (R_2O_3)	0.15	1.14
Calcium oxide (CaO)	53.78	54.61
Magnesia (MgO)	1.19	0.22
Combined alkalies ($K_2O + Na_2O$)	0.77	0.56
Sulphuric anhydride (SO_3)	trace	trace
Loss by ignition	43.15	42.79
Lime calculated to calcium carbonate ($CaCO_3$)	96.08	97.52

[a] Analyzed by Forrest B. Beyer.

Binangonan limestone is the more available to Manila because of the more difficult water transportation or the expense of the necessary railroad transportation from Montalban to Manila. In either place there is an abundant supply of almost pure limestone within 30 kilometers of Manila.

The siliceous materials in the vicinity of Manila vary greatly in chemical and physical properties, but after careful consideration we were able to select 8, so that the variety included the principal characteristics of all of probable importance. Their character and usefulness will be discussed in conjunction with their location.

Beach sand.—South of Manila there is no stream entering the Bay which contains deposits of sand. Between 12 and 14 kilometers from Manila at Sangley Point and at Las Piñas, with which there is water communication, beach sand is abundant. This sand is derived principally from basaltic rocks which occur fragmentally in the tuff formation which borders Manila Bay. The grains are in an advanced stage of decomposition and are easily crushed. The Manila beach itself at Maytubig has similar, but very fine, sand from which fairly good sand-lime bricks have been manufactured. The efficiency of this fine beach sand is of more than ordinary importance because it is the only available siliceous material which is fine enough to require no grinding, and also because it is so abundant and easily procured. This work was completed before property owners near Maytubig protested against the removal of sand. Now a supply will have to be obtained from a greater distance or dredged from the bay.

TABLE VII.—*Maytubig beach sand and its efficiency as a sand-lime brick material.*

Description and classification.	Content of silica (SiO_2).			
	Soluble in hydrochloric acid (HCl).	Soluble in sodium carbonate (Na_2CO_3).	Free silica or quartz.	Total silica.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
A very fine-grained sand containing magnetite, considerable partly kaolinized feldspar, and a little quartz. The grains of magnetite, pyroxene, and hornblende are generally rounded, and those of feldspar and quartz angular	0.37	14.86	2.61	60.51

TABLE VII.—*Maytubig beach sand and its efficiency as a sand-lime brick material*—Continued.

CHARACTERISTIC GRANULARIMETRIC COMPOSITION.									
Standard sieve No.	10	20	30	40	50	60	80	100	200
Meshes per linear inch	10	20	30	40	50	60	80	100	200
Diameter of openings in millimeters	1.85	0.92	0.56	0.47	0.34	0.28	0.20	0.15	0.06
Percentage of sand passing through specified sieves	100.0	100.0	99.9	99.7	98.0	96.5	89.4	51.7	6.0

THE SAND-LIME BRICK.

Mixture No.	Fineness of sand as used.	Dimensions of brick.	Area of bearing surface.	Duration of steam treatment.	Molding pressure per square inch.	Compressive strength.	
						Total.	Per square inch.
		Inches.	*Sq. in.*	*Hours.*	*Pounds.*	*Pounds.*	*Pounds.*
1	As received	2×2×2	4.0	5.5	4,600	7,200	1,800
2	One-fourth pulverized	2×2×2	4.0	5.5	4,600	7,720	1,930
1	As received	2×2×2	4.0	8.0	10,640	13,880	3,470
2	One-fourth pulverized	2×2×2	4.0	8.0	10,640	11,200	2,800
3	One-tenth pulverized	3×3×2.25	6.75	8.0	10,000	20,560	ᵃ 3,200
3	____do	3×3×2.25	6.75	8.0	15,000	25,920	3,840
4	As received	2×2×2	4.0	8.0	7,640	8,000	2,000
4	____do	2×2×2	4.0	8.0	10,000	13,360	ᵇ 3,340

Mixture No.	Molding pressure in pounds per square inch	Density.		Absorption after 24 hours in water.	
		Air dry.	Dried at 110°.	Air dry.	Dried at 110°.
4	10,000	2.08	2.01	7.40	11.0

ᵃ Plate III, fig. 2, is a photograph of the finished product.
ᵇ Plate IV, fig. 2, is a photograph of the finished product after an attempt had been made to polish the front surface. This brick had a density (air-dried) of 2.08 and it absorbed 7.4 per cent by weight of water after being submerged for twenty-four hours.

In all instances, the bricks had a pleasing steel-gray color which after several months' exposure to sun and rain had not changed, but the surface would not take a good polish.

Pasig sand.—Most of the sand used in Manila is dredged or dipped up in baskets from the Pasig and its principal tributary, the Mariquina River. A good sand-lime brick can be made with this sand, but the supply is rapidly decreasing owing to the great quantity used for concrete construction work.

Table VIII.—*Pasig sand and its efficiency as a sand-lime brick material.*

Description and classification.	Content of silica.			
	Soluble in hydrochloric acid (HCl).	Soluble in sodium carbonate (Na$_2$CO$_3$)	Quartz.	Total silica.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
A clean, rounded, pebble sand derived principally from andesite and basaltic rocks. Quartz is present in amounts up to 12 per cent, and iron minerals are also more or less abundant. The prevailing color is a dark slate..	0.18	18.43	11.20	62.72

GRANULARIMETRIC COMPOSITION.

Sieve No. -----------------------	10	20	30	40	50	60	80	100	200
Per cent of sand passing through specified sieves ---- {	ᵃ99.5	99.0	95.0	71.0	36.0	20.5	10.0	2.0	trace
	ᵇ96.0	64.0	42.0	38.0	23.5	10.0	5.0	2.6	trace

THE SAND-LIME BRICK.

Mixture No.	Degree of pulverization in per cent through specified sieves.					Duration of steam treatment.	Molding pressure per square inch.	Compressive strength.	
	No. 20.	No. 40.	No. 80.	No. 100.	No. 200.			Total.	Per square inch.
						Hours.	*Pounds.*	*Pounds.*	*Pounds.*
5	100.0	84.0	55.4	46.5	18.6	5.5	2,300	5,980	1,495
5	100.0	84.0	55.4	46.5	18.6	5.5	4,600	10,800	2,700
6	89.4	57.7	23.7	16.5	11.7	8.0	7,640	12,720	3,180
6	89.4	57.7	23.7	16.5	11.7	8.0	10,000	13,640	3,410
ᶜ7	91.6	65.8	33.7	24.7	13.2	8.0	7,640	17,000	4,250
7	91.6	65.8	33.7	24.7	13.2	8.0	10,000	21,280	5,320
8	99.6	72.9	40.4	37.4	20.0	8.0	7,640	19,040	4,760
8	99.6	72.9	40.4	37.4	20.0	8.0	10,000	23,740	5,935

Mixture No.	Molding pressure in pounds per square inch.	Density.		Absorption after 24 hours in water.	
		Air dry.	Dried at 110°.	Air dry.	Dried at 110°.
7	7,640	2.24	2.15	6.1	10.5
7	10,000	2.28	2.19	4.8	9.7
ᶜ8	7,640	2.23	2.13	5.2	10.1
8	10,000	2.30	2.17	3.6	9.4

ᵃ Dipped up in baskets.   ᵇ Gravel screenings from dredges.   ᶜ Ground finer than No. 6.

Strong and dense sand-lime bricks are much more readily obtained with Pasig than with beach sand, and this is especially

true when the molding pressure is low. The color of the product is darker and less pleasing, but the bricks made took a fairly good polish, due largely to the presence in quantity of large grains of andesite and basalt rock, as is shown by the granularimetric analysis of mixture 6. Fig. 1, Plate V, is a photograph of a 3 by 3 by 2.25-inch brick made from mixture 6. The front surface had been polished. Fig. 6, Plate VII, is a photograph of a brick made from mixture 7 and shows the perfect soundness after the brick had been subjected to the fire test.

The Pasig sand used in the above experiments contained very little iron, and, thus far, the surface of the bricks has not shown signs of rust stains. Sand from some parts of the Mariquina River contains large quantities of iron, and the use of such material should be avoided.

The granularimetric analyses of mixtures 6, 7, and 8 show a graduated increase in the degree of pulverization and a corresponding increase in strength. A comparison of the granularimetric analysis of the sand as used in mixture 8 with that of the sand as it is received shows that considerable grinding is necessary in order to obtain great strength. However, we have a large quantity of very fine beach sand near at hand, and grinding expenses can be reduced to a low figure by mixing this with coarser available siliceous materials. The lower initial cost of beach sand would also make the production more economical. The results given in Table IX for an equal mixture of Pasig and beach sand were obtained without grinding any of the siliceous materials. A still better product would have been obtained had the beach sand been ground a little before mixing.

TABLE IX.—*Sand-lime bricks made with equal parts of Pasig and beach sand.*[a]

Mix-ture No.	Granularimetric composition of mixed sands in per cent passing through the specified sieves.					Duration of steam treat-ment.	Molding pressure per square inch.	Compressive strength.	
	No. 20.	No. 40.	No. 80.	No. 100.	No. 200.			Total.	Per square inch.
						Hours.	Pounds.	Pounds.	Pounds.
9	.99.8	75.7	54.8	27.2	3.2	8.0	7,640	10,720	2,680
9	99.8	75.7	54.8	27.2	3.2	8.0	10,000	13,760	3,440

[a] Plate VII, fig. 2, shows the perfect soundness of one of these bricks after it had been subjected to the fire test.

TABLE IX.—*Sand-lime bricks made with equal parts of Pasig and beach sand*—Continued.

Mixture No.	Molding pressure in pounds per square inch.	Density.		Absorption after 24 hours in water.	
		Air dry.	Dried at 110°.	Air dry.	Dried at 110°.
9	7,640	2.14	2.08	7.7	10.5
9	10,000	2.16	2.10	6.5	9.2

Quingua sand.—North of Manila, the Quingua River contains an important amount of pebble sand which is similar to Pasig sand, except that the grains are harder and the quartz a little more abundant. The distance from Manila is considerable (about 35 kilometers), and although transportation by water is possible the river is often too shallow for navigation by launches. Transportation by rail is possible, but the present rates are prohibitive. This sand has not been tested, but its similarity to Pasig sand and greater content of quartz make it certain that it is equally as good, if not better.

Tarlac sand.—Sand from the Tarlac River, at Tarlac, a station situated on the Manila and Dagupan railroad, appears to be the best sand-lime brick sand in Luzon. Owing to the large percentage of quartz and clear glassy plagioclase feldspar, Tarlac sand-lime bricks have a pleasing grayish-white color, and take a good polish with a sparkling, granitic appearance. So far as we have been able to ascertain, there need be no efflorescence even when the percentage of feldspar is as high as in this material. The best results in our simple tests of the fire-resistant properties of Philippine sand-lime bricks were obtained when Tarlac sand was used. Figs. 1 and 4, Plate VII, are photographs of sand-lime bricks made from mixtures 11 and 12, respectively, which remained sound after the fire test. Transportation from Tarlac to Manila must be largely by railroad, and the present high rates are prohibitive.

TABLE X.—*Tarlac sand and its efficiency as a sand-lime brick material.*

Description and classification.	Content of silica.			
	Soluble in hydrochloric acid (HCl).	Soluble in sodium carbonate (Na2CO3)	Quartz.	Total silica.
	Per cent.	Per cent.	Per cent.	Per cent.
A clean, sharp, mottled-gray sand which contains magnetite, basalt, olivine, and about 50 per cent of clear, glassy grains readily mistaken for quartz, but which are in reality mostly plagioclase feldspars _____	0.06	11.82	2.91	66.07

TABLE X.—*Tarlac sand and its efficiency as a sand-lime brick material*—Continued.

GRANULARIMETRIC COMPOSITION.

Sieve No.	10	20	30	40	50	60	80	100	200
Percentage of sand passing through specified sieves	98.5	74.0	41.0	22.0	11.5	6.5	3.5	1.5	0.5

THE SAND-LIME BRICK.

Mixture No.	Degree of pulverization in per cent through standard specified sieves.					Duration of steam treatment.	Molding pressure per square inch.	Compressive strength.	
	No. 20.	No. 40.	No. 80.	No. 100.	No. 200.			Total.	Per square inch.
						Hours.	*Pounds.*	*Pounds.*	*Pounds.*
10	100.0	85.0	71.0	59.0	20.0	5.5	2,300	7,000	1,750
10	100.0	85.0	71.0	59.0	20.0	5.5	4,600	10,060	2,515
11	89.3	24.6	18.3	17.7	10.7	8.0	7,640	13,040	3,260
11	89.3	24.6	18.3	17.7	10.7	8.0	10,000	13,640	3,410
12	99.9	60.5	33.8	26.5	20.5	8.0	7,640	13,880	3.470
12	99.9	60.5	33.8	26.5	20.5	8.0	10,000	15,920	3,980
a13	99.9	68.4	40.3	34.9	29.6	8.0	7,640	21,180	5,295
13	99.9	68.4	.40.3	34.9	29.6	8.0	10,000	25,960	6,490

Mixture No.	Molding pressure in pounds per square inch.	Density.		Absorption after 24 hours in water.	
		Air dry.	Dried at 110°.	Air dry.	Dried at 110°.
12	7,640	2.19	2.11	3.8	7.5
12	10,000	2.24	2.17	2.4	5.7
13	7,640	2.22	2.16	2.1	5.0
13	10,000	2.29	2.23	1.7	4.1

a Ground finer than No. 12.

As with Pasig sand, the natural coarseness of Tarlac sand makes considerable grinding advisable; however, beach sand can be advantageously mixed with the more expensive sand. This, as well as the manner in which the strength of a given mixture may be affected by the quantity of water used, is shown in Table XI.

TABLE XI.—*Sand-lime brick made with a mixture of equal parts of Tarla and beach sand.*

Mix-ture No.	Degree of fineness in per cent through the specified sieves.					Per-cent-age of water added to the raw mate-rials.	Molding pressure per square inch.	Compressive strength.			Remarks.
	No. 20.	No. 40.	No. 80.	No. 100.	No. 200.			Total.	Per square inch.	
							Pounds.	*Pounds.*	*Pounds*	
a 14	95.7	62.1	49.4	33.7	8.4	8.0	7,640	7,920	1,980	No water was pressed out during the molding.
14	95.7	62.1	49.4	33.7	8.4	8.0	10,000	13,360	3,340	
b 15	95.7	62.1	49.4	33.7	8.4	15.0	7,640	14,040	3,510	About 10 per cent of the water was pressed out during the molding.
15	95.7	62.1	49.4	33.7	8.4	15.0	10,000	16,620	4,155	

Mixture No.	Molding pressure in pounds per square inch.	Density.		Absorption after 24 hours in water.	
		Air dry.	Dried at 110°.	Air dry.	Dried at 110°.
15	7,640	2.11	2.09	6.5	7.7
15	10,000	2.19	2.14	4.9	7.5

a A comparatively dry mixture.   b A comparatively wet mixture.

Fig. 5, Plate VII, is a photograph of a brick made from mixture 15, after it had been subjected to the fire test. It remained perfectly sound.

Orani sand.—At the mouth of the Orani River, about 55 kilometers northwest of Manila and directly across Manila Bay, there is an abundance of good sand which can be secured without dredging. The river can be entered by launches, and at low tide the sand can be loaded directly into barges and, without rehandling, towed to Manila. Orani sand is very similar to that from Tarlac except that it is less clean and its color is less attractive. Otherwise, it is as good as Tarlac sand for the manufacture of sand-lime bricks. We obtained a strength of 3,238 pounds per square inch with Orani sand when the molding pressure employed was only 4,600 pounds per square inch.

Volcanic tuff, unusually abundant in Bulacan and along the Pasig River, especially near Guadalupe, is another available source of siliceous material in the vicinity of Manila. It is a fragmental material which contains pieces of scoria, basaltic pebbles, and volcanic ash in varying and nonuniform proportions, and it is easily crushed. When mined, it is so soft that it can be quarried with an ax, but it hardens rapidly on exposure to the air. There are two grades of this water-laid

tuff: (1) coarse, containing numerous fragments of pumice and andesite; and (2) very fine, containing grains of pumice, feldspar, hornblende, and, at times, a little quartz. Our tests include Meycauayan, the best, and Guadalupe, the ordinary volcanic tuff.

TABLE XII.—*Volcanic tuff and its efficiency as a sand-lime brick material.*

Source.	Content of silica.			
	Soluble in hydrochloric acid (HCl).	Soluble in sodium carbonate (Na₂CO₃)	Quartz.	Total silica.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Guadalupe	0.98	20.45	0.00	59.72
Meycauayan	0.02	21.04	2.08	56.99

Mixture No.	Volcanic tuff used.	Degree of pulverization in per cent passing through the specified sieves.					Duration of steam pressure.	Molding pressure per square inch.	Compressive strength.	
		No. 20.	No. 40.	No. 80.	No. 100.	No. 200.			Total.	Per square inch.
							Hours.	*Pounds.*	*Pounds.*	*Pounds.*
16	Guadalupe	100.0	85.0	70.0	50.0	28.5	5.5	2,300	9,000	2,250
16	____do ____	100.0	85.0	70.0	50.0	28.5	5.5	4,600	10,300	2,575
17	____do ____	91.3	71.1	44.4	38.0	25.5	8.0	7,640	10,480	2,620
17	____do ____	91.3	71.1	44.4	38.0	25.5	8.0	10,000	13,640	3,410
18	Meycauayan	68.5	44.9	28.4	23.5	13.0	8.0	7,640	12,440	3,110
18	____do ____	68.5	44.9	28.4	23.5	13.0	8.0	10,000	12,960	3,240
19	____do ____	70.5	48.3	31.2	26.0	17.8	8.0	7,640	18,140	4,535
19	____do ____	70.5	48.3	31.2	26.0	17.8	8.0	10,000	20,140	5,035
20	____do ____	83.3	61.2	38.2	32.5	20.2	8.0	7,640	20,720	5,180
20	____do ____	83.3	61.2	38.2	32.5	20.2	8.0	10,000	22,050	5,520
21	Guadalupe	100.0	82.6	62.8	55.0	41.0	8.0	7,640	14,920	3,730
21	____do ____	100.0	82.6	62.8	55.0	41.0	8.0	10,000	18,280	4,570

Mixture No.	Molding pressure in pounds per square inch.	Density.		Absorption after 24 hours in water.	
		Air dry.	Dried at 110°.	Air dry.	Dried at 110°.
20	7,640	1.87	1.75	6.0	13.4
20	10,000	1.89	1.77	5.9	13.0

Fig. 1, Plate VI, is a photograph of a 3 by 3 by 2.25-inch brick of mixture 18, which was taken after an attempt had been made to polish the front surface. A good polish could not be obtained, and, otherwise, the natural color was a rather unpleasing, dull, light-brown.

Fig 3, Plate VII, is a photograph of a sand-lime brick made

from mixture 19. The cracks were caused by shrinkage due to the tendency of volcanic tuff to flux and melt at the maximum temperature used. In spite of its cracked condition, this brick withstood a pressure of 3,400 pounds per square inch (240 kilograms per square centimeter).

A high content of soluble silica, such as is characteristic of these volcanic tuffs, favors the development of great strength. On the other hand, most of the individual grains are soft, and soft grains are detrimental to the strength. For best results the volcanic tuff should be mixed with hard-grained sands or crushed rock, and for this purpose it is especially adapted both on account of the high content of soluble silica and the ease with which it can be obtained, pulverized, and molded for a maximum strength.

TABLE XIII.—*Sand-lime brick made with a mixture of 1 part of pulverized Guadalupe stone and 3 of natural Pasig sand.*

Mixture No.	Degree of fineness in per cent through the specified sieves.					Duration of steam treatment.	Molding pressure per square inch.	Compressive strength.	
	No. 20.	No. 40.	No. 80.	No. 100.	No. 200.			Total.	Per square inch.
						Hours.	*Pounds.*	*Pounds.*	*Pounds.*
22	99.0	79.0	32.5	26.0	16.5	8.0	7,640	13,200	3,300
22	99.0	79.0	32.5	26.0	16.5	8.0	10,000	13,600	3,400

The advisability of using volcanic tuff or beach sand in conjunction with other available siliceous materials rather than alone is further substantiated by the fact that the sand-lime bricks made from either alone possess the least density and absorb the most water.

Quarry débris is also available. The amount of rock and crushed stone used in Manila for breakwaters, macadam roads, and concrete is considerable, and at present 4 quarry sites are operated to meet the demand; namely, (1) the Rizal, (2) the Manila city quarries at Talim Island, (3) Carabao Island quarry in the south channel entrance of Manila Bay, and (4) the Sisiman quarry near Mariveles.

Crusher-run Sisiman stone contains a large amount of rock flour and sand which is not suitable for road surfacing on account of its poor cementive value. At present this quarry débris is a waste product. Sisiman rock is a gray andesite, while the stone in the other quarries is basalt. Neither contains free silica, but both are high in soluble silica. Owing to this high content

of soluble silica and the hardness of the individual grains, sand-lime brick of the best quality can be manufactured from them. Both materials are especially suited for the manufacture of tiles and ornamental stonework. This is more or less apparent from fig. 2, Plate VI, and fig. 1, Plate IV, which are photographs of 3 by 3 by 2.25-inch sand-lime bricks made from Sisiman and basaltic rock, respectively, although these photographs fail to show the glossiness of the polished front surfaces. The bricks photographed were made from mixtures 22, Table XV, and 23, Table XVI, and it should be borne in mind that, in order to obtain a glossy surface and granitic appearance, the stones were not ground to the degree of fineness necessary to give a high strength. Nevertheless, it is safe to assume that beautiful, polished, dense "artificial marbles" can be made with these materials without reducing the strength below 4,000 pounds per square inch.

TABLE XIV.—*Available quarry débris.*

Rock.	Classification.	Content of silica.			
		Soluble in hydrochloric acid (HCl).	Soluble in sodium carbonate (Na₂CO₃).	Quartz.	Total silica.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Sisiman rock from Mariveles.	A gray andesite which contains no free silica or quartz.	0.37	23.59	0.00	54.77
Basalt rock from Talim Island.	A dark, dense, basaltic rock which shows practically no crystalline structure to the unaided eye and contains no quartz.	1.00	21.17	0.00	54.73

TABLE XV.—*Sand-lime brick made from Sisiman rock quarry débris.*

Mixture No.	Degree of pulverization in per cent passing through the standard specified sieves.					Duration of steam treatment.	Molding pressure per square inch.	Compressive strength.	
	No. 20.	No. 40.	No. 80.	No. 100.	No. 200.			Total.	Per square inch.
						Hours.	*Pounds.*	*Pounds.*	*Pounds.*
22	73.4	48.2	29.4	25.3	16.5	8.0	7,640	10,960	2,740
22	73.4	48.2	29.4	25.3	16.5	8.0	10,000	16,120	4,030

Mixture No.	Molding pressure in pounds per square inch.	Density.		Absorption after 24 hours in water.	
		Air dry.	Dried at 110°.	Air dry.	Dried at 110°.
23	10,000	2.22	2.15	4.4	7.5

TABLE XVI.—*Sand-lime brick made from basalt rock quarry débris.*

Mixture No.	Degree of pulverization in per cent passing through the standard specified sieves.					Duration of steam treatment.	Molding pressure per square inch.	Compressive strength.	
	No. 20.	No. 40.	No. 80.	No. 100.	No. 200.			Total.	Per square inch.
						Hours.	*Pounds.*	*Pounds.*	*Pounds.*
23	75.6	43.7	25.8	22.9	17.0	8.0	7,640	12,080	3,020
23	75.6	43.7	25.8	22.9	17.0	8.0	10,000	15,280	3,820

Mixture No.	Molding pressure in pounds per square inch.	Density.		Absorption after 24 hours in water.	
		Air dry.	Dried at 110°.	Air dry.	Dried at 110°.
23	10,000	2.34	2.28	3.8	6.1

Transportation from the Talim Island quarry, which is near
Binangonan, involves only water transportation and costs under
fairly economic administration about 1.15 pesos per cubic meter.
At the present time the price of crushed stone from Talim is
2.70 to 2.90 pesos per cubic meter at the Manila water front.
Sisiman is directly across the bay, and, although about 55 kilo-
meters from Manila, the cost of transportation should not be
prohibitive as it would be entirely over deep water. At present,
crushed stone from Sisiman costs 3.50 pesos at the Manila water
front, but as the quarry débris is a waste product it should cost
much less. These costs are so much higher than Pasig sand,
which can be purchased for 97 centavos, or less, and the cheaper
beach sand, that the manufacturer probably would care to use
the crushed rock only for special purposes such as tiles and
marble, for which it is especially adapted. However, the cost
of production can be retained at a normal figure by mixing the
quarry débris with beach sand or crushed volcanic tuff. The
latter can be quarried at Guadalupe and transported to the Pasig
River for about 43 centavos per cubic meter.

PLANT SITE IN MANILA.

We believe that an economic scheme for utilizing the materials
in the vicinity of Manila would be to locate a sand-lime brick
plant on the bank of the Pasig River adjacent to the volcanic
tuff, and bring limestone from Binangonan. This plan would
avoid a long haul to the factory of supplies such as fuel, machinery,

and operating necessities, and put the finished product in close communication with the railroads, and, by short water route, with the ships in the harbor, while close at hand would be the volcanic tuff, and the sands from Pasig, Mariquina, Pasay, and Manila Bay.

The advantages of Manila as a location are all those which accrue from proximity to the main port and largest city of the Philippines. The disadvantages are: (1) the transportation of the limestone over a distance of 7 kilometers by land and 17 by water; (2) the lack of natural protection at Binangonan where an anchorage must be provided for floating stock against severe storms which occasionally sweep Laguna de Bay; and in all probability, (3) the impossibility of using the best sand (Tarlac sand) on account of prohibitive freight rates.

OTHER PLANT SITES.

Although at present Manila appears to be the most suitable place for a sand-lime brick plant, other localities should be given thorough consideration. It is possible that the Visayan Islands and Mindanao will develop more rapidly than the rest of the Philippines, and the growing importance of Cebu, Iloilo, Zamboanga, and Jolo as ports may eventually make a central location more desirable than Manila.

Cebu.—As yet we have made very few sand-lime bricks from raw material other than those already reported. However, some of the important considerations involved have been thoroughly covered by Wallace E. Pratt, of this Bureau, in a recent report[15] on the available raw materials and locations for the Portland cement industry. This and other available information indicate that the vicinity of Cebu, Cebu, the second city in size and importance in the Archipelago, would be a suitable central location for the industry. Large deposits of subbituminous coal occur on the Island of Cebu near the seaport towns of Danao and Naga. Danao is situated 38 kilometers north and Naga 19 kilometers south of Cebu City with which they have railway as well as water connection. Mr. Dalburg of this Bureau has recently estimated that the coal from the Uling field can be delivered at Naga at a cost of 5 pesos per ton, and that at least 800,000 tons are available. The analyses given in Table

[15] *Min. Resources P. I. for 1911, Bur. Sci., Div. Min.* (1912), 111.
114047——4

XVII show that both the Uling and Danao coal should rank among good limekiln coals, as they are high in hydrogen and volatile constituents, low in ash, sulphur, and fixed carbon, and sufficiently high in calorific value.

TABLE XVII.—*Calorific value and proximate analyses of Cebu coals.*

Constituent.	Danao coal from Camansi mine, average of many samples.	Naga coal from Uling mine.		
		Lower ledge No. 1.	Lower ledge No. 2.	Upper coal.
Moisture	10.01	14.90	11.85	19.23
Volatile combustible matter	a37.93	38.63	38.67	35.44
Fixed carbon	46.30	41.91	45.37	39.10
Ash	5.76	4.56	4.08	6.53
Sulphur	0.77	0.35	0.39	0.43
Calorific value in calories:				
With moisture	6,071	5,744	6,017	5,800
Dry	6,746	6,840	6,897	6,676

a Hydrogen=5.90 per cent.

It further appears that sandstone, sand, and limestone of good quality are available in quantity. All the necessary raw materials, including coal, can be found in large quantities about 11 kilometers up the Danao River. The upper coal seams are covered with a sandstone formation varying in thickness up to about 6 meters, and large deposits of soft coralline and hard, pure, calcite limestone are in the immediate neighborhood. The ultimate chemical composition of available sand- and limestone is given in Table XVIII.

TABLE XVIII.—*Analyses of raw materials near Danao.*

Constituent.	Sandstone.	Limestone.	Coralline limestone.
Silica (SiO_2)	72.76	0.38	2.61
Aluminium and ferric oxides (R_2O_3)	15.53	0.18	2.23
Calcium oxide (CaO)	1.42	55.62	52.85
Magnesia (MgO)	0.62	0.00	0.88

Baguio, Benguet.—The lack of local building materials and the great expense of importing the same into the mountain capital of the Philippine Islands has led many to advocate the establishment of a sand-lime brick plant at Baguio. Limestone and soft,

easily crushed sandstone are available in abundance, and some of this material has produced the very best quality of sand-lime brick.

TABLE XIX.—*Sand-lime brick made from Benguet sandstone.*

Mix-ture No.	Siliceous material.	Dimensions of brick.	Area of bearing surface.	Compressive strength.	
				Total.	Per square inch.
		Inches.	Sq. in.	Pounds.	Pounds.
25	Benguet sandstone No. 1	3×3×2.25	6.75	32,215	4,772
26	Benguet sandstone No. 2	3×3×2.25	6.75	49,410	a7,320

a Plate V, fig. 2, is a photograph of a brick obtained from this mixture. The front surface has been polished and the color is a very pleasing cream-gray, spotted with quartz. The density of this brick was 1.82 (air-dried), and it absorbed 4.35 per cent of water when submerged for 24 hours.

Aside from the fitness of available raw materials, the possibility of successful, commercial manufacture of sand-lime bricks in this locality involves complicated and uncertain financial considerations.

FINANCIAL CONSIDERATIONS.

In Germany the average cost of manufacturing common sand-lime brick is approximately 6 pesos (3 dollars United States currency) per thousand,[17] and in America the average cost is about 8 pesos for common, and 9 pesos for face, brick. An idea of the cost of manufacture under favorable and unfavorable conditions may be obtained from estimates which were presented to the First Annual Convention, National Association Manufacturers of Sand Lime Products.[18] One estimate which considers coal at 8.50 pesos per ton, lime at 1.60 pesos per barrel (185 pounds, net), and sand at 1.20 pesos per cubic yard, put the cost of manufacture at 10 pesos per thousand. Another placed the total cost at 7.20 pesos per thousand, allowing for slack coal at 2.90 pesos per ton and lime at 80 centavos per barrel. E. C. Eckel[19] has estimated the cost of manufacture at a small plant (10,000 bricks per twenty-four hours), where sand was obtain-

[17] Consul-General Skinner, *U. S. Daily Consular and Trade Reports*, Bureau of Manufactures (1911), No. 9.

[18] *Clay Workers* (1904), 42, 582–591.

[19] Cements, Limes and Plasters. New York (1905), 141.

able at nearby beds, but where lime and coal were expensive. His estimate is as follows:

Item.	Dollars.
Lime, 1.5 tons, at 8 dollars,	12.00
Coal, 1.5 tons, at 4.25 dollars,	6.38
Labor, 6 men,	8.75
Superintendent and office expenses	10.00
Repairs, supplies, etc.	2.00
Interest, depreciation, etc.	6.00
Cost per 10,000 bricks	45.13
Cost per thousand	4.51

A more detailed estimate of the cost of manufacturing 40,000 bricks per day is given by Peppel [20] as follows:

Equipment.

Item.	Dollars.
Land and buildings	15,000
1 wet-pan	1,000
1 ball-mill	500
2 presses	4,400
2 pug-mills	800
Conveyors	6,000
Shafting and belting	3,000
1 100-horsepower Corliss engine	2,500
2 100-horsepower boilers	2,000
1 25-horsepower boiler	300
4 hardening-cylinders, 7 by 60 feet,	8,000
Erecting and insulating cylinders	1,000
Pipes for preliminary heating	1,000
Railroad tracks, etc.	4,500
Total	50,000

Cost of manufacture, 40,000 bricks.

Item.	Dollars.
Sand, 157 cubic yards, at .07 dollar,	11.00
Lime, 11 tons, at 4 dollars,	44.00
Coal, 3 tons, at 2.25 dollars,	6.75
Repairs	5.00
Oil and grease	3.00
Labor, 40 men, at 1.35 dollars,	54.00

[20] *Trans. Am. Ceramic Soc.* (1902), 4.

Cost of manufacture, 40,000 bricks—Continued.

Item.	Dollars.
Fireman, at 2.50 dollars,	2.50
Office expenses	20.00
Depreciation and interest, 12 per cent,	20.00
Total	166.25
Selling expenses, 10 per cent,	16.00
Cost of manufacturing 40,000 bricks	182.25
Cost of bricks per thousand	4.55

These figures show the manner in which the cost of manufacture is influenced by local conditions such as the cost of fuel, labor, supplies, machinery, building, raw materials, quality of bricks produced, etc. They also show that the cost of production can be maintained at a comparatively low figure in spite of rather unfavorable conditions.

In the Philippines, fuel for burning the limestone and for generating power is certain to be expensive even if local coal is used unless it is found practicable to locate the limekilns near a mine or an available source of firewood. Other items for which higher costs must be allowed, as compared with practises in the United States and Germany, are first cost of plant, administrative supervision, plant depreciation, repairs, supplies, and transportation by land. More definite information in this respect will be combined with an estimate of the cost of manufacturing sand-lime brick at the suggested site on the Pasig River. This estimate is based on a plant having a capacity of 20,000 bricks in twenty-four hours, and 10,000 pesos additional is allowed for extra machinery and molds for building blocks, tiles, ornamental products, etc. The cost of machinery and supplies is about 25 per cent more than the average price in the United States where ordinarily a well-equipped sand-lime brick plant with a daily capacity of 20,000 bricks costs, independent of site and building, about 40,000 pesos. To this sum of 60,000 pesos, 10,000 pesos are added for a large factory site, and 10,000 pesos for buildings. This brings the total cost of the plant to 80,000 pesos. Three estimates, including our own, of the amount of labor and raw materials required for 20,000 bricks are given in Table XX.

TABLE XX.—*Estimates of the amount of labor and raw materials for a daily production of 20,000 bricks.*

Labor and materials.	Common bricks.		9-inch bricks of best quality with an average equipment.
	International Sand-lime Brick and Mfrg. Co., Melbourne, Australia.[a]	Ideal Brick Machinery Co., New York City.[b]	Bureau of Science.
Foreman	1		1 (European or American).
Engineer	1	1	1 (Filipino).
Fireman	1	1	Do.
Common laborers	8	12	14 (Filipinos).[c]
Sand or crushed stone	[d]52 tons	[d]42.5 tons	70 tons = 60 cubic yards = 46 cubic meters.
Quicklime or its equivalent in hydrated lime.	3.0 tons	3.0 tons	6.0 tons = 10 per cent slaked lime.
Coal or its equivalent in wood, gas, or oil.	8.0 tons	2½ tons to 4 tons.	3.0 tons.

[a] *Cem. & Eng. News* (1911), **23**, 130.

[b] Sand-Lime Bricks and Blocks: Ideal Brick Machinery Co., New York City.

[c] This figure includes men for handling the sand, lime, and bricks.

[d] We consider that the above estimates of 52 and 42.5 tons of sand are much too low as the average weight of good sand-lime bricks is about 8 pounds. Likewise, the lime estimates of 3 tons must be regarded as inadequate for a uniform, good product. Our estimates for sand and lime are higher than is necessary for common brick. They are based on the requirements of face brick.

The economic problems involved in the cost of quarrying, dredging, transportation, and manufacture, and the more vital one of obtaining the best results in the use of the materials is beyond the scope of this paper. For this reason an estimate on the minimum cost of production is impossible, but a careful consideration of local conditions has enabled us to make a fairly accurate estimate. In Manila common laborers receive from 80 centavos to 1 peso per day. For the purpose of this estimate their efficiency is rated at one-half that of American or European workmen. Salaries for foreign technical men are from 15 to 30 per cent higher in Manila than in the United States, but good Oriental engineers and firemen are available at comparatively low wages. It is probable that a local sand-lime brick industry would have to depend on coal imported from Japan or Australia for fuel.[21] The price of this coal in Manila

[21] Recently Borneo crude oil such as is used in gas engines has been purchased on the Manila market for 0.0462 peso per liter. It is sold in drums of 295 liters, and samples tested showed 10,515 total calories and an available heating value of 9,712 calories.

varies from 9.50 pesos to 10.50 pesos per metric ton. Good coal for generating power and burning limestone can be obtained, but a careful selection is necessary as shown by the analyses given in Table XXI.

TABLE XXI.—*Analyses* [a] *of typical coals received in Manila since December 1, 1910.*[b]

Numbers, except as otherwise indicated, represent percentage.

	Japan.			Australia.		Borneo.	
	Miike nut.	Moji Yamano lump.	Karatzu Ochi lump.	New-castle Seeham "Best screen-ed."	New-castle Browns Duck-enfield Mer-thyr.	Labuan.	Cowie Harbor, British North Borneo. (Air dried.)
Percentage of fine coal (through ⅜-inch mesh)	97.71	40.50					
Percentage of slack (through ¼-inch mesh)	19.64	12.60					
Number of tons in cargo	2,740	1,000	3,400	3,830	5,021	1,791	
Proximate analysis:							
Moisture	0.43	1.83	2.32	2.56	2.41	c 6.14	1.01
Volatile combustible matter	41.45	38.85	39.65	35.08	33.69	43.76	42.68
Fixed carbon	47.59	43.39	47.59	51.96	53.65	46.21	39.42
Ash	10.53	15.93	10.44	10.40	.10.25	3.89	16.89
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Sulphur (separately determined)	2.00	1.61	1.01	0.51	0.96	0.48	
Coking quality	coking	coking	coking	coking	coking	noncoking	
Available heating value in calories by calorimeter	c 7,402	6,408	6,627	6,711	6,640	6,508	

[a] Analyses by Forrest B. Beyer.

[b] Cox, A. J., *This Journal, Sec. A* (1912), 7, 4.

[c] Miike coal has the highest calorific value, but its easily fusible ash and high content of sulphur are detrimental to its efficiency.

The cost of manufacturing sand-lime brick would be excessive if the manufacturer paid the prevailing Manila market prices for lime. One merchant quoted 30 pesos per ton for quicklime which is considerably more than the cost of Portland cement. Another submitted figures on poor material of local manufacture which were equivalent to air-slaked rock lime at 17.08 pesos per ton. This high market value is largely due to the crude process of local manufacture and to the small and

irregular demand.[22] A steady demand of 3 tons per day would probably lower the price to not more than 25 per cent in excess of the average cost in the United States or Europe. An estimate of 16 pesos per ton for good quicklime is reasonably high.

According to the above estimates the maximum cost of manufacturing 20,000 sand-lime bricks daily and selling expenses would be as follows:

Item.	Pesos.
Interest on investment at 8 per cent (300 working days per year)	21.32
Foreman (American or European),	8.00
Engineer (Filipino),	4.00
Fireman (Filipino),	2.00
Laborers (Filipinos), 18, at 90 centavos,	16.20
Sand, 46 m³ (70 tons), at 97 centavos,	44.62
Lime, 6 tons, at 16 pesos,	96.00
Coal, 3 tons, at 10 pesos,	30.00
Oil and waste	4.00
Wear and tear	10.00
Total	236.14
Selling expenses at 10 per cent	23.62
Cost of manufacturing 20,000 bricks	259.76
Cost of manufacturing 1,000 bricks	13.00

This estimated cost of 13 pesos per thousand 9-inch face bricks is based on liberal operating expenses. Good management and the installation of limekilns ought to reduce the cost below 11 pesos, and a further saving of raw materials would result from the manufacture of hollow bricks and building blocks. However, even a cost of 13 pesos per thousand is reasonably cheap when compared with the local price of other materials of the same class. Concrete construction work is expensive. At the water front, cement costs from 4.50 to 5.50 pesos per barrel; gravel, 1.80 to 2.20; sand, 0.98 to 1.20; and crushed stone, 2.70 to 3.50 pesos per cubic meter. Prepared cement and clay products are even more expensive, as shown by the following prices furnished by the Bureau of Supply under date of August 14, 1912.

[22] The value of lime imported into the Philippine Islands during the years 1907 to 1911 averaged only 920 pesos annually. When imported from foreign countries it is subjected to a customs tariff of 8 centavos per 100 kilograms.

TABLE XXII.—*Manila prices of clay and cement products.*

Article.	Dimensions.	Cost.
	Inches.	
Common brick (soft)	From 8.25×3.9×1.8 to 9×4.4×2	25 pesos per thousand and up.
Fire brick	8.9×4.4×3.1	89 pesos per thousand and up.
Floor tiles (glazed)	12×12	77 pesos per thousand and up.
Vitrified clay water pipe	10×24	2.904 pesos each.
Do	8×24	1.470 pesos each.
Do	4×24	0.660 peso each.
Cement floor tiles	12×12	From 30 to 77 pesos per 1,000.
Cement water pipes	12 (diameter)	0.907 peso per linear foot.
Do	8×36	1.034 pesos per linear foot.

In the United States, "the average price per thousand received for common sand-lime brick was $6.36 in 1910, as compared with $6.39 in 1909, and $6.33 in 1908; for front brick $10.90 as against $11.98 in 1909, $12.16 in 1908, and $10.96 in 1907."[23] In Manila the market value ought to be much greater, but, according to our estimate of the cost of producing front brick, even the above selling prices should leave a good margin of profit.

SUMMARY.

1. In the Philippines conditions are very favorable for the manufacture of brick and artificial stone from sand and lime if the enterprise is carefully and conservatively managed. The selection of a factory site, raw materials, process of manufacture, and machinery should receive unusual care.

2. The best location for the first plant is probably in the vicinity of Manila. Tests and information concerning the available raw materials indicate the advantages of locating a sand-lime brick plant near the Pasig River at Guadalupe.

3. The cost of manufacturing and selling 20,000 9-inch bricks of the best quality is estimated not to exceed 13 pesos (6.50 dollars United States currency) per thousand. Compared with other Philippine building materials of equal value this is very reasonable, and the profit of a plant could be increased by extending its operations to include the manufacture of lime, hollow building blocks, tiles, slabs, marbles, ornamental stones, etc.

[23] *Min. Resources U. S. Geol. Surv.* (1910), 626.

ILLUSTRATIONS.

PLATE I.

A segment of a reinforced beam of reconstructed stone.

PLATE II.

An exhibit of reconstructed stones and marbles at the 1907 Building Trades Exhibition, Olympia, England.

PLATE III.

FIG. 1. A sand-lime brick which disintegrated during the hardening process on account of the presence of unslaked, free lime.
2. Sand-lime brick made from Maytubig beach sand (*cf.* mixture 3, Table VII).

PLATE IV.

FIG. 1. Sand-lime brick made from Talim quarry, basalt rock (*cf.* mixture 23, Table XVI).
2. Sand-lime brick made from Maytubig beach sand (*cf.* mixture 4, Table VII).

PLATE V.

FIG. 1. Sand-lime brick made from Pasig sand (*cf.* mixture 6, Table VIII).
2. Sand-lime brick made from crushed Benguet sandstone (*cf.* mixture 25, Table XIX).

PLATE VI.

FIG. 1. Sand-lime brick made from Meycauayan volcanic tuff (*cf.* mixture 18, Table XII).
2. Sand-lime brick made from Sisiman quarry andesite rock (*cf.* mixture 22, Table XV).

PLATE VII.

Sand-lime bricks made from Philippine raw materials, heated to 1,100° and plunged into water.
FIG. 1. Coarsely ground. Tarlac sand, brick mixture.
2. Brick mixture containing equal parts of Pasig and beach sand. ·
3. Volcanic tuff, brick mixture.
4. Finely ground. Tarlac sand, brick mixture.
5. Brick mixture containing equal parts of Tarlac and beach sand.
6. Pasig sand, brick mixture.

PLATE VIII.

Common sand-lime brick made from Philippine raw materials. (Upper, *cf.* mixture 10, Table X; lower, *cf.* mixture 16, Table XII.)
FIG. 1. Before subjection to crushing in the compression test.
2. After subjection to crushing in the compression test.

. TEXT FIGURE.

FIG. 1. Map of the vicinity of Manila (1 millimeter equals 1 kilometer).
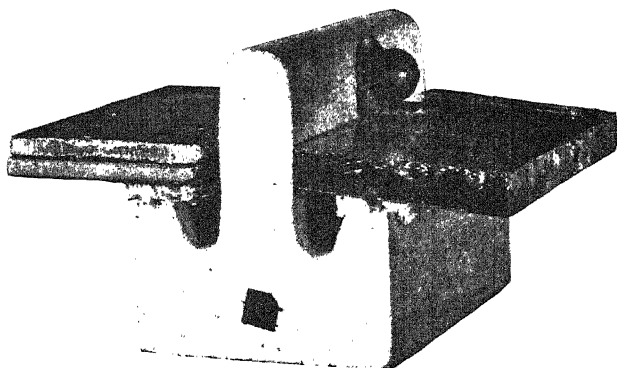
PLATE I.   SEGMENT OF A REINFORCED BEAM OF RECONSTRUCTED STONE.
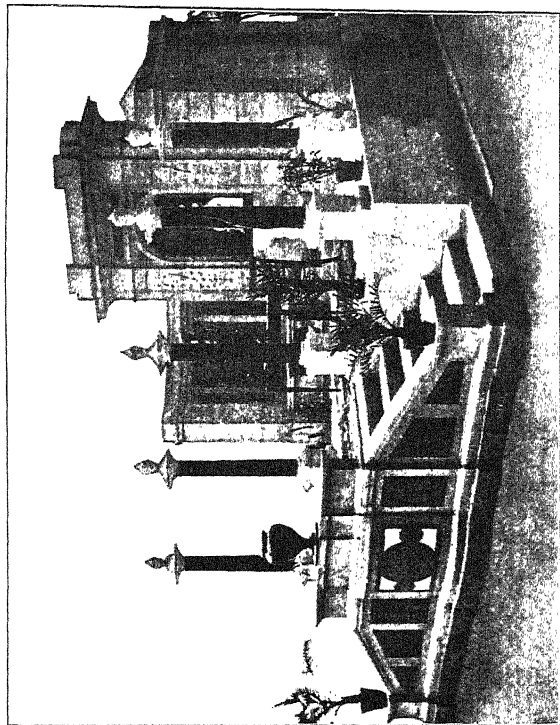
PLATE II. RECONSTRUCTED STONES AND MARBLES.
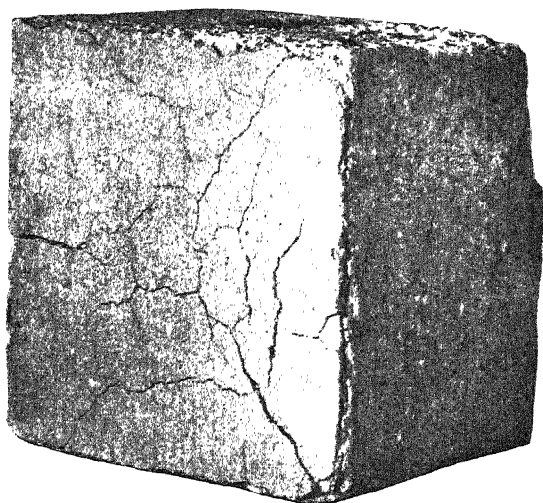
Fig. 1.   Sand-lime brick disintegration caused by the hydration of free lime during the
hardening process.
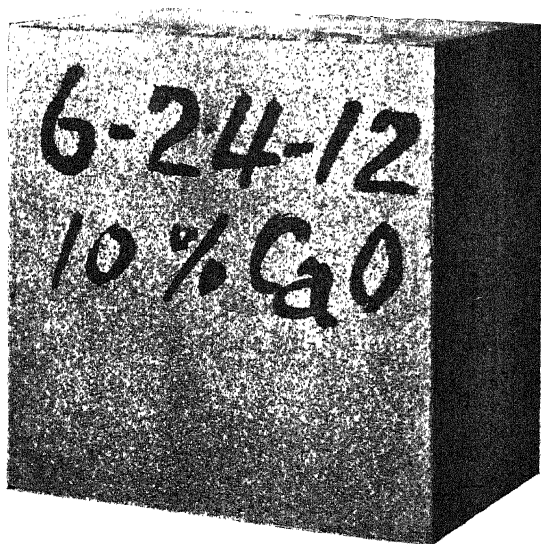
Fig. 2.   Maytubig beach sand, brick mixture.
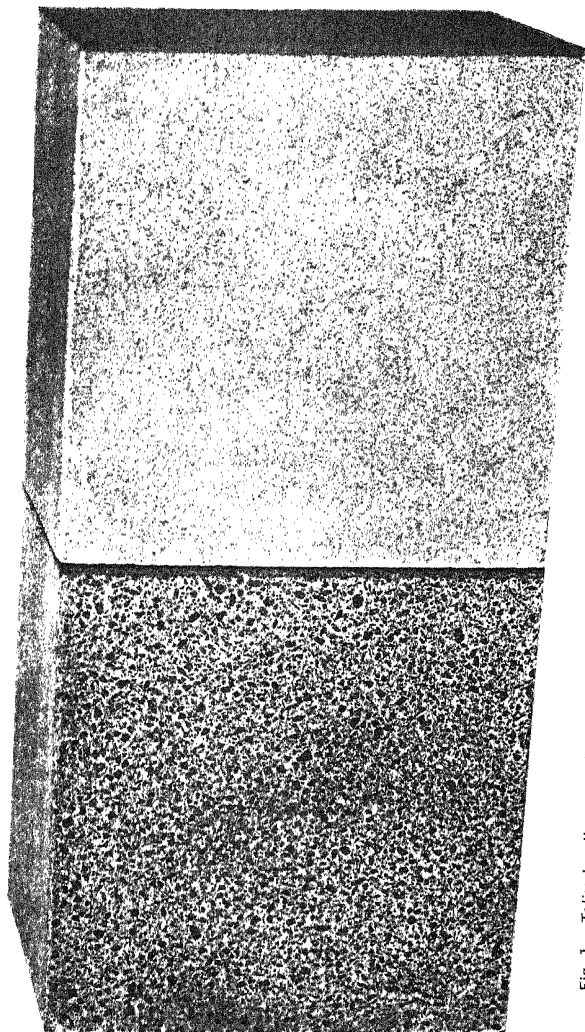
PLATE III.

Fig. 1. Talim basalt quarry débris, brick mixture.

Fig. 2. Maytubig beach sand, brick mixture.

PLATE IV.
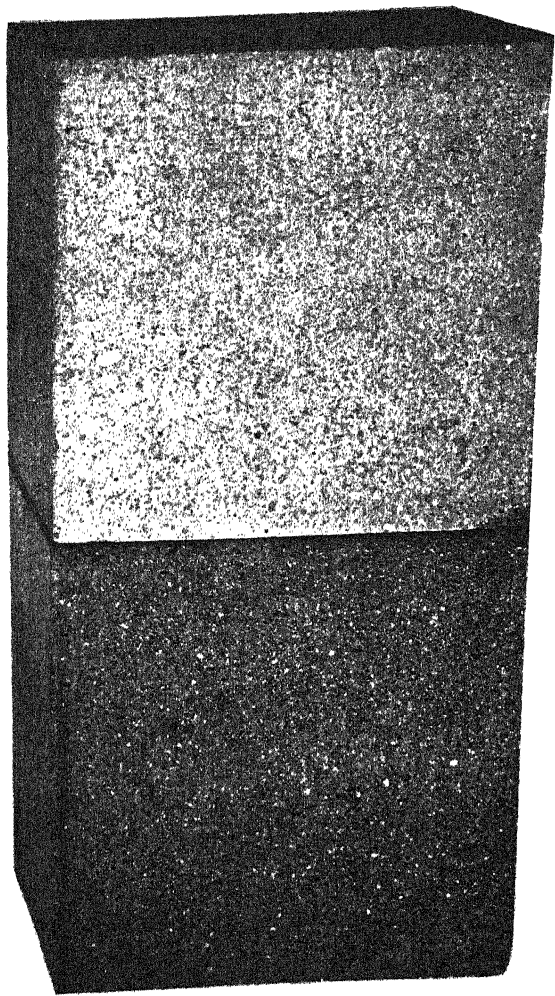
Fig. 1. Pasig sand, brick mixture.

Fig. 2. Benguet sandstone, brick mixture.

PLATE V.
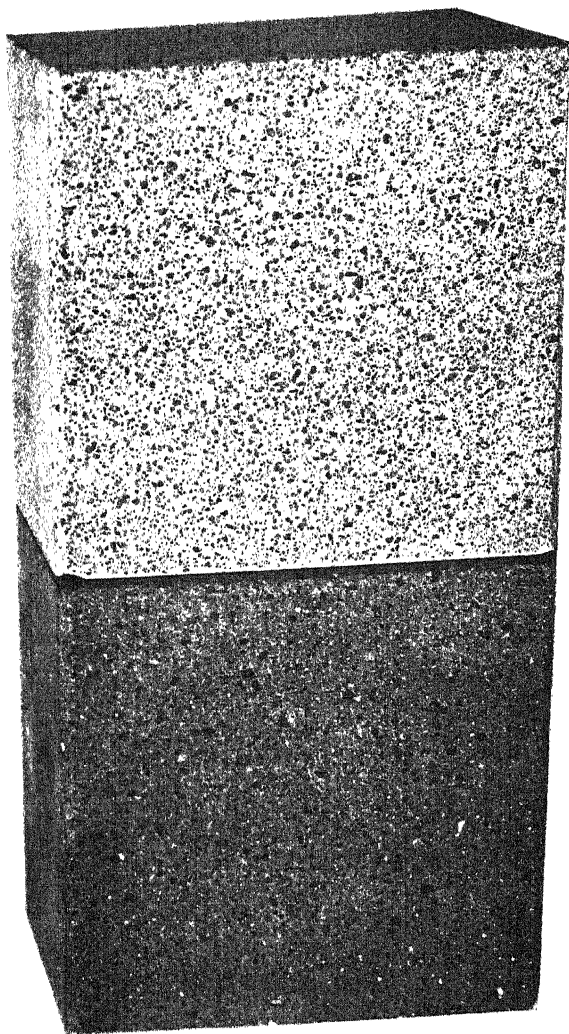
Fig. 1. Meycauayan volcanic tuff, brick mixture.

Fig. 2. Sisiman andesite quarry débris, brick mixture.

PLATE VI.
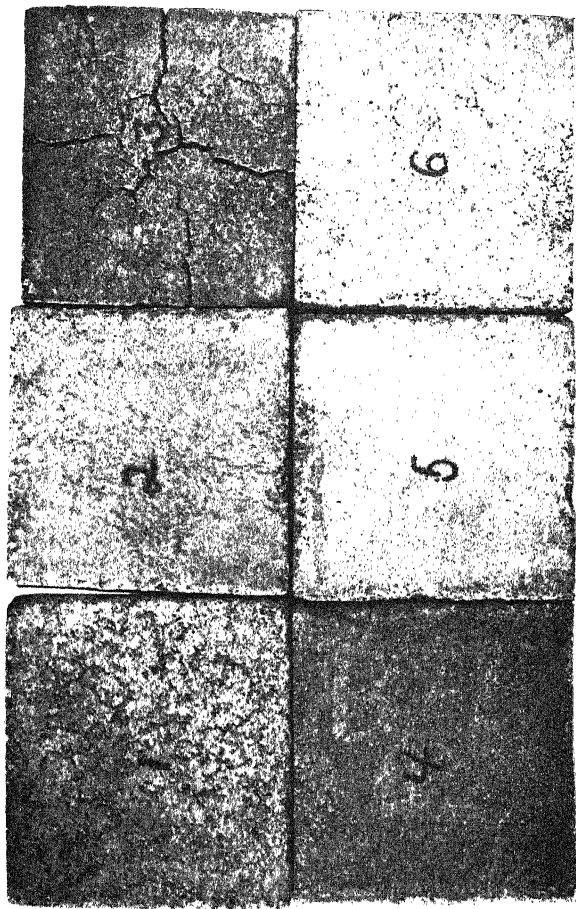
PLATE VII. SAND-LIME BRICKS MADE FROM PHILIPPINE RAW MATERIALS, HEATED TO 1,100° AND PLUNGED INTO WATER
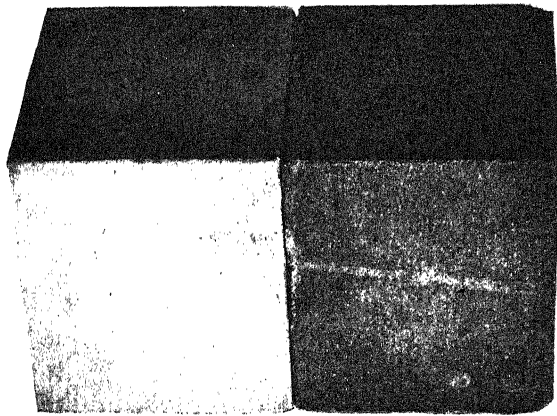
Fig. 1.
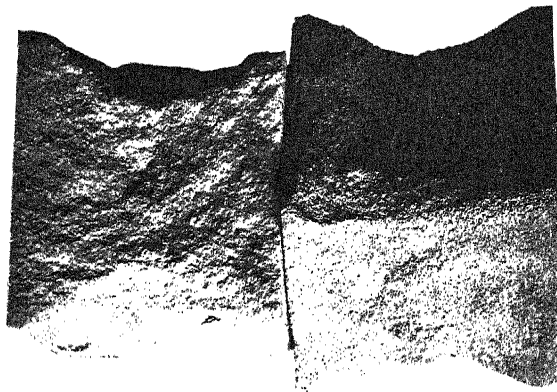
Fig. 2

PLATE VIII.   COMMON SAND-LIME BRICK (PHILIPPINE RAW MATERIALS)   BEFORE AND AFTER CRUSHING.

EXTRACTION TEST OF A MODERN SUGAR CENTRAL.

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INTRODUCTION.

The primary object of this paper is to place before the sugar manufacturers in the Philippine Islands some reliable data on the operation and efficiency of a modern central of the smaller type working under conditions such as are met with in pioneer work where exact control is hindered through lack of laboratory facilities, skilled workmen, weighing facilities, etc. At present these conditions are more or less inevitable. For this reason we report results which were obtained when average, rather than exceptionally good, conditions of manufacture prevailed. By doing this we believe that our conclusions concerning the advantage of refining sugar by small centrals over the older and commoner methods now in vogue will be much more reliable and convincing than a similar but more spectacular treatise based upon theoretical or ideal conditions. The results included in this report were obtained under very disadvantageous circumstances, but they are considered accurate enough for the purpose involved and of value to sugar producers of whom the majority in the Islands at this time are not acquainted with central factory methods.

DESCRIPTION OF THE PLANT.

Our tests were made during a four-day run of a small modern central located at Muntinlupa, Rizal Province. It is a small mill with a capacity of about 100 tons of cane per day of twenty-four hours, and was designed by the Harvey Engineering Company of Glasgow.

The crushing portion consists of a 3-roller mill and crusher, the latter being of the conical groove type. It is fitted with a cane carrier and bagasse feeder which are operated by 2 horizontal, return tube boilers, arranged with step-grates for burning green bagasse. A reciprocating, slide valve engine is used to drive the mill and carriers. A plunger pump is attached to the

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main drive shaft of the engine, and elevates the raw juice to 2 liming tanks on the top floor. The juice is here limed to excess, using phenolphthalein as the indicator, and then allowed to flow downward through the sulphur box, where the excess alkali is neutralized by sulphur fumes which are drawn up through the box from a sulphur stove by means of a steam injector placed on the top. From this point the juice flows through a juice heater, employing exhaust steam, into 5 settling tanks or subsiders. After settling, the clear juice is run into the eliminators, which are circular tanks supplied with heating coils. After elimination, the juice is raised to the evaporator supply tank by a duplex pump. The slums, both from the settling tanks and the eliminators, are run into a slum tank where they are limed, heated, and pumped to the 2 filter presses. Three evaporators of the standard type are used for concentrating the thin juice. The thick juice is pumped from the third evaporator into 3 thick-juice storage tanks on the pan floor. The sirup is drawn from here into the pan by vacuum and boiled down to grain. The pan is of the usual type with a capacity of 4 tons of massecuite, or approximately 2 tons of sugar per strike.[1] It is fitted with 2 heating coils, which may be used with either live or exhaust steam. The pan and evaporators have separate vacuum pumps, an arrangement which allows one to be used independently of the other, thus avoiding fluctuations in vacuum. The massecuite is dropped from the pan into a mixer of equal capacity which is supplied with a shaft having paddles attached. This shaft turns slowly and prevents the sugar of the massecuite from dropping to the bottom of the mixer, while at the same time allowing an even growth of crystals when it is deemed advisable to use the mixer as a crystallizer. A spout leads from the bottom of the mixer to 2 Weston centrifugal machines, run at a speed of 1,500 revolutions per minute by means of a small auxiliary engine that also serves to turn the mixer shaft and the rotary molasses pump. The molasses from the machines is pumped to the pan floor into 2 molasses blowup tanks, where it is diluted to 28° Baumé (D=1.2361), reboiled, and sent to the second sugar tanks where the sugar crystallizes out. After a few days the second massecuite is ready to be centrifuged. The molasses from this may be considered as final or discard molasses, or it may be boiled again to what is technically known as "string proof," and then allowed to stand a number of months,

[1] The weight of sugar from a pan may run from 45 to 60 per cent of the weight of the massecuite, depending on the boiler.

when the sugar which has crystallized out is centrifuged. In all cases the sugar is collected from under the machines, mixed, and sacked ready for the market.

The sizes and capacities of the different parts are as follows:

Mill rollers, 20×30 inches (51×75 cm.).
Boilers, 80 horsepower each.
Engine for mill 11×24 inches (27.5×60 cm.).
Engine for centrifuges 7×10 inches (17.5×25 cm.).

	Cubic feet.	Hecto-liters.
Liming tanks (2) each	24	6.8
Subsiders (5) each	33	9.38
Eliminators (2) each	42	12
Evaporator supply (1)	46	13
Pan storage, thick juice (3)	64	18
Molasses blowup (2)	108	31
Evaporators (3), approximately,	50	14
Second sugar tanks (6)	81	23
Discard molasses (1)	6,000	1,700

Pan (1), 4 tons (3,637 kilograms).
Mixer (1), 4 tons (3,637 kilograms).
Centrifugal machines 24″ (60 cm.).
Filter presses (2), 24 frames, 24×24 inches (61×61 cm.).

METHOD OF HARVESTING THE CANE.

The cane fields were situated about 4 kilometers from the mill. A small 3-ton locomotive was used to haul the cane in 1-ton cars from the fields to the mill. A 0.61-meter (24-inch) track with rails weighing 9 kilograms per meter (20 pounds per yard) was used on this tram line. Six cars were in the field being loaded with cane, 6 en route to the factory, and 6 at the mill being unloaded, with 2 extra cars for auxiliaries. More cars would have facilitated transportation and increased the output of sugar. Movable track was laid in the fields as close to the cane as convenient. When the distance became too great for economical handling by hand, 6 bull carts were employed to continue the loading. Approximately 50 men were used in the field for stripping, cutting, and loading. By this system about 5 tons of cane per hour could be delivered at the factory.

CONDITIONS AND RESULTS OBTAINED FROM THE MILL TEST.

Our tests covered a run of four days when the conditions of manufacture and the results obtained were as follows:

The conditions of manufacture were such as to make the extraction low and the losses high. The cane was long overripe so that it contained considerable invert sugar, and the working crew was new and inexperienced, making overheating of the juice and other wasteful practises common occurrences. The mill operated under less than full capacity with no attempt to crush at night, and a comparatively small amount of sugar was introduced, as the quantity of cane crushed during the run amounted to only 113,840 kilograms.[a]

Facilities for weighing both the cane and the juice were not available, so that the quantity of sugar introduced was determined volumetrically; that is, by measuring the hot juice in the settling tanks or subsiders, correcting this volume for temperature, and ascertaining the percentage of sucrose. The results obtained are recorded in Table I.

TABLE I.—*Sugar introduced.*

Time.	Raw juice.		Subsider juice.			
	Brix.	Purity.	Brix.	Purity.	Sugar.	Quantity.
					Per cent.	*lbs.*
First day, April 29, 1912	22.6	83.0	23.5	84.0	19.7	
	22.0	83.8	23.6	83.8	19.8	
	22.8	83.5	23.4	84.2	19.7	
	23.0	83.6	23.7	84.0	19.9	
	22.6	83.5	23.5	84.0	19.8	175.6
Second day, April 30, 1912	22.9	81.6	23.6	82.8	19.5	
	22.5	82.7	23.5	82.6	19.4	
	22.3	82.5	23.4	83.0	19.4	
	23.1	82.0	23.7	82.7	19.6	
	22.8	82.2	23.6	82.8	19.5	175.6
Third day, May 1, 1912	22.4	81.0	24.8	82.6	20.4	
	23.0	82.0	24.6	82.7	20.4	
	22.8	81.8	25.0	83.0	30.8	
	23.1	82.0	24.7	82.7	20.4	
	22.8	81.8	24.8	82.8	20.5	194.8
Fourth day, May 2, 1912	21.6	80.7	24.0	82.0	19.7	
	21.9	81.0	23.8	82.2	19.5	
	21.5	80.5	24.2	81.8	19.8	
	22.0	81.6	24.1	81.9	19.7	
	21.7	81.1	24.0	82.0	19.7	222.1
Four days, average	22.4	82.2	24.0	82.8	19.8	
Total						768.1

[a] Estimated by considering juice extraction at 75 per cent.

The figures in Table I show a total introduction of 768.1 hectoliters of raw juice. Each hectoliter weighed 99.8 kilograms, making a total weight of 76,658 kilograms; and as the sucrose content of the juice measured was 19.8 per cent, the quantity of 100-per-cent sugar introduced into the mill during the four-day run amounted to 15,178.4 kilograms.

During this time the plant produced 13,076 kilograms of sugar averaging 98.4 per cent sucrose which, based on a purity of 100 per cent, amounts to 12,866 kilograms. These figures were obtained by weighing all of the sugar sacked from each strike and polarizing average samples. All of the data are given in Table II.

TABLE II.—*Production of mill.*

Time.	Thick juice.		Massecuite.		Molasses.		Sugar produced.	
	Brix.	Purity.	Brix.	Purity.	Brix.	Purity.	Sucrose.	Weight.
							Per cent.	*Kilos.*
First day, April 29, 1912.	62.2	80.3						
	62.5	80.1						
	62.0	80.0	90.0	71.9	75.0	54.2	98.5	1,649
	62.1	80.0	93.4	67.8	80.0	40.8	98.1	1,864
	62.2	80.1	91.7	69.8	77.0	47.5		3,513
Second day, April 30, 1912.	60.8	79.1						
	61.0	79.8						
	60.9	79.9	92.0	79.5	78.0	49.0	98.5	2,200
	60.5	79.9	90.6	73.5	80.5	45.1	97.6	1,645
	60.8	79.7	91.3	76.5	79.3	47.1		3,845
Third day, May 1, 1912	63.0	79.0						
	62.8	79.5						
	60.0	79.4						
	63.5	79.8	92.4	74.4	78.0	49.0	97.6	1,784
	62.3	79.7	92.4	74.4	78.0	49.0		1,784
Fourth day, May 2, 1912.	62.5	80.4						
	61.2	81.2						
	62.9	79.9	90.0	71.6	80.0	44.2	99.0	2,091
	63.0	79.9	92.4	71.8	81.0	45.8	98.1	1,863
	62.5	80.4	91.2	71.7	80.5	45.0		3,954
Four days, average	61.9	80.0	91.8	73.1	78.8	47.1	98.4	
Total								13,076
Calculated							100.0	12,866

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Obviously, in order to ascertain the percentage yield of the sugar introduced, it was necessary to ascertain the quantity of available sugar in the process before and after the run. The data in Tables III and IV give this information as "available sugar," and the values indicated signify the yield of 100-per-cent sugar which the amount of sugar in process was capable of producing on a basis of 40-per-cent molasses.

TABLE III.—*Sugar in process at the beginning of the run.*

Juices.	Brix.	Puri-ty.	Sugar.	Quan-tity.	Kilos per hecto-liter.	Total weight of juices.	Total weight of sug-ar.	Avail-able sugar.	Sugar in mo-lasses.
			P. ct.	*Hls.*		*Kilos.*	*Kilos.*	*Kilos.*	*Kilos.*
Thin juice	23.3	84.0	19.6	52.9	109.2	5,787	1,136	997	159
	24.5	84.0	20.5	8.7	109.8	959	196	169	27
Thick juice	55.4	80.0	45.8	26.4	125.8	3,321	1,521	1,241	280
Second sugar	90.0	71.9	67.8	13.6	148.1	2,019	1,370	1,068	302
Total							4,223	3,455	768

TABLE IV.—*Sugar in process at the end of run including molasses discard.*

Juices.	Brix.	Puri-ty.	Sugar.	Quan-tity.	Kilos per hecto-liter.	Total weight.	Total weight of sug-ar.	Avail-able sugar.	Sugar in mo-lasses.
			Per ct.	*Hls.*		*Kilos.*	*Kilos.*	*Kilos.*	*Kilos.*
Molasses discard			46.0			4,391			2,020
Molasses sirup	71.4	51.1	41.0	25.5	135.2	3,466	1,418	709	709
Do	80.0	61.0	44.1	30.6	142.0	4,350	1,919	1,264	656
Total							3,337	1,973	3,385

The difference between 3,455 and 1,973, or 1,482 kilograms, represents the amount of 100-per-cent sugar extracted from the sugar in the process which was not introduced during the run. Therefore, this difference of 1,482 must be deducted from the total yield of 12,866 kilograms, leaving 11,382 kilograms as actual yield from the sugar introduced during the run. The figures in Table V summarize the results so far obtained.

TABLE V.—*Data on factory conditions during run.*

Item.	Quantity.		
	By weight.	Based on cane crushed.	Based on sugar introduced.
	Kilos.	*Per cent.*	*Per cent.*
a. Cane crushed during run	113, 840	100. 00	750. 00
b. Sugar in process at the beginning of run	3, 455	3. 02	22. 65
c. Available sugar in process at the end of run	1, 973	1. 75	12. 95
d. Reduction of available sugar in process during run (*b—c*)	1, 482	1. 27	9. 70
e. Sugar introduced during run	15, 178	13. 34	100. 00
f. Yield of sugar during run	12, 866	11. 27	84. 70
g. Yield obtained from sugar introduced during run (*f—d*)	11, 384	10. 00	75. 00
h. Loss of sugar during process of manufacture (*e—g*)	3, 794	3. 34	24. 99

According to the figures in Table V, the loss of sugar during the process of manufacturing amounted to 24.99 per cent of the sugar introduced. We also determined the loss by measuring the quantity and polarizing average samples of molasses and by weighing and sampling the cake issuing from the filter presses. The results obtained are tabulated in Tables VI and VII, and are summarized in Table VIII.

TABLE VI.—*Loss of sugar in molasses.*

Item.	Quantity.		
	By weight.	Based on cane crushed.	Based on sugar introduced.
	Kilos.	*Per cent.*	*Per cent.*
i. Sugar in discard molasses and molasses in process at end of run.	3, 385	2. 96	22. 24
j. Sugar in molasses in process at beginning of run	768	0. 67	5. 05
k. Sugar lost in molasses during the run (*i—j*)	2, 617	2. 29	17. 19

TABLE VII.—*Loss in the filter presses.*

Item.	First day.	Second day.	Third day.	Fourth day.	Total.
					Kilos.
Number of presses in use	4	4	4	4	
Average weight of mud cake in kilograms per frame	13. 18	13.68	14.09	14. 52	
Percentage of sugar in cake	14. 5	15. 1	15. 2	15. 8	
Total number of frames	96	96	96	96	
Total weight of mud cake in kilograms	1, 264.3	1, 313. 3	1, 352. 6	1, 393. 9	
Total weight of sugar lost in kilograms	183. 4	197. 0	205. 4	213. 1	798. 9
Estimated loss of sugar in skimmings from slum tank					263. 1
Grand total					1, 062. 0

TABLE VIII.—*Total loss of sugar.*

Item.	By weight.	Quantity.	
		Based on cane crushed.	Based on sugar introduced.
	Kilos.	*Per cent.*	*Per cent.*
k. Sugar lost in molasses during run	2,617	2.29	17.19
l. Sugar lost in press skimmings during run	1,062	0.93	6.96
m. Determined loss (*k + l*)	3,679	3.22	24.15
h. Calculated loss	3,794	3.34	24.99
n. Undetermined loss (*h—m*)	115	0.12	0.84

The high loss of sugar in molasses was to be expected on account of the low purity of the original juice. In spite of this the total loss of 24.99 per cent is abnormally large for a mill of this type and is to be attributed to the faulty design and overworking of the clarification system which caused an unusually large amount of mud and juice to be sent to the slum tank and presses. This is apparent from the fact that a normal loss in filter presses is less than 1 per cent, while here it amounts to 6.96 per cent. The increased extraction which would result from proper changes in this part of the mill is readily apparent.

COMPARISON OF THE NEW WITH THE OLD PROCESS OF MANUFACTURE.

From the data of the tests made by Walker,[a] in Negros, the writers have calculated that approximately 83 per cent of the total sugar introduced could have been obtained as raw sugar by the old process if the same crushing mill as described above had been used and operated with the same filter-press losses. There were 15,178 kilograms of sugar introduced, and 83 per cent of this amounts to 12,595 kilograms, or 208 piculs. On account of the low purity of this cane (82.2 per cent), the best that could be expected of the sugar obtained by the native process would be *"Humedo,"* which has a grading of from 75- to 79.9-per-cent sugar. In all probability, the product would run *"Corriente"* which polarizes below 75 per cent. However, we will assume that *"Humedo"* is produced and that this is worth 4 pesos (2 dollars United States currency) per picul when No. 1 sugar (87 per cent sugar and over) is worth 7 pesos. Then the sugar made by the native process would be worth 808 pesos.

By the central process of manufacture we obtained 11,384 kilo-

[a] The Sugar Industry in the Island of Negros. Manila (1910).

grams or 182 piculs of 100-per-cent sugar, or 190 piculs of 96°
sugar. At 9 pesos per picul (the price that could be obtained
for this grade when the native No. 1 is worth 7 pesos),[4] this
would be worth 1,710 pesos. Furthermore, as it costs about
3 pesos per picul to raise and produce the native sugar, and
about 4.5 pesos to raise and produce the central sugar, the re-
spective margins of profit would be in accordance with the fol-
lowing figures:

	Native process (pesos).	Central process (pesos).
Cost	606.00	855.00
Receipts	808.00	1,710.00
Difference	202.00	855.00

It is evident that, compared with the central process, the old
process gives a very low and unsatisfactory margin of profit when
the cane is not of the best quality.

If the purity of the cane had been such as to allow No. 1 sugar
to be made by the native process, the sugar could have been sold
for 7 pesos per picul. The approximate figures then would be:

	Native sugar (pesos).	Central sugar[a] (pesos).
Cost	606.00	855.00
Receipts	1,414.00	1,710.00
Difference	808.00	855.00

[a] These are very low figures, since no allowance has been made for increased yield of
sugar due to the increased purity of the cane. This would increase the extraction by about
8 per cent of the available sugar.

These figures show that when high-grade sugar can be made,
the old process gives about as satisfactory returns as a small
central. However, dependence can not be placed on the quality
of sugar produced by the native process. It may run No. 1
or No. 5, and the chances are in favor of the latter. In some
districts the purity of the cane always runs high to the profit
of the planters, but in the majority of instances the purity runs
low, and as a result, and in spite of the use of skilled workmen,
inferior sugar is produced at a small margin of profit. On the
other hand, our results show that even when the conditions of
manufacture and the quality of cane are poor, the modern sugar
central produces a high-grade sugar at a comparatively low cost.

[4] There is no definite difference between the price offered for 96° centrifu-
gal and No. 1 native sugar, but the former is generally worth at least
2 pesos more than the latter.

Market conditions make this certainty of the quality of the product a consideration of great importance. During periods of sugar shortage, the poor sugars are easily sold, but, when centrifugal sugars can be bought at a reasonable price, the refiners no longer care for the native type of sugar regardless of its quality. The yield decreases and the cost of refining increases with a decrease in purity, and the refiners prefer to pay a slightly higher price for sugar which can be refined without difficulty and give good yields, rather than work up poor material with their higher grade products. Furthermore, it becomes more and more difficult for them to dispose of the raw molasses as the sugar content and purity of the sugar refined decreases.

In view of these facts it appears that the installation of centrals throughout these Islands is greatly to be desired from every point of view, and, as the cost of installation is small compared with the benefits obtainable, we heartily indorse their erection and use. An estimate of the cost and installation of a central factory designed to deliver 160 piculs of sugar per day, with cost of maintainance for a one-hundred-day campaign is briefly as follows:

Cost of equipment.

Item.	Pesos.
Mill, machinery, and buildings	80,000.00
Erection	20,000.00
Shop and tools	4,000.00
Laboratory	2,000.00
Three kilometers of tram	8,000.00
Two locomotives	8,000.00
Cane wagons	8,000.00
	130,000.00

Cost of production.

Item.	Pesos.
Salaries	7,500.00
Transportation	8,000.00
Wages	4,000.00
Sundries	2,500.00
Packing	2,000.00
Commissions	3,500.00
Depreciation	4,000.00
Improvements	4,000.00
Interest	6,500.00
To manufacture 1,000 tons of sugar	42,000.00
Cost per ton	42.00
Cost per picul	2.62

If transportation to the United States is included in the cost of production, the cost per picul will be increased to 3.25 pesos.

CONCLUSIONS.

Our test of a modern central was made when the cane was overripe, the workmen inexperienced, and the filter process overworked. In spite of these and other disadvantages of pioneer work, the plant produced a high grade of sugar (98.4 per cent) and a yield which, figured on a basis of 100-per-cent sugar, amounted to 75.01 per cent of the sugar introduced. The results obtained are low for a central, but even so the margin of profit is sufficient to show the great superiority of modern methods of sugar refining over the prevailing native process.

Moreover, the conditions of the sugar market are rapidly becoming such that the old process will soon fail to give profitable returns. It is wasteful and can not be depended upon to produce a No. 1 sugar, whereas with the central process the best quality of sugar can always be produced, and a high-grade sugar is the only quality from which satisfactory profits can be expected.

In view of these facts, the authors urge the immediate installation of modern methods of sugar refining, and it is their firm belief that unless this is done the local sugar industries will suffer serious losses in the near future.

ILLUSTRATION.

Fig. 1.　A carabao mill.

Fig. 2.　A modern sugar mill.
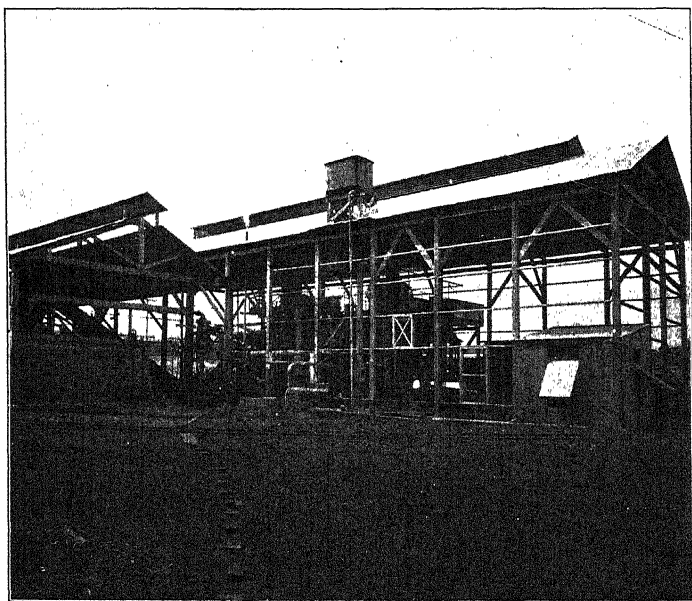
PLATE I.

THE ABSORPTION SPECTRA OF ORTHO- AND PARA-NITROPHENOL AND PARA-NITROSOPHENOL.

NEW EVIDENCE OF THE QUINOID STRUCTURE OF THESE COMPOUNDS IN ALKALINE SOLUTION.

By H. D. GIBBS[1] and D. S. PRATT.

(From the Laboratory of Organic Chemistry, Bureau of
Science, Manila, P. I.)

Baly, Edwards, and Stewart[2] described the absorption spectra of the three nitroanilines, the three nitrophenols, and *p*-nitrosophenol, and from their investigations of these compounds in neutral, acid, and alkaline solutions conclude that, in alkaline solutions, they all exist in the quinoid form. Four years later, Baly, Tuck, and Marsden[3] entirely retract the first explanation of the color of the nitroanilines and the salts of the nitrophenols, and substitute the explanation that the change from a colorless compound to a colored one or a deepening of the color of a colored compound of this type is not due to any essential change in structure, but merely to a shift of an absorption band from the invisible to the visible region of the spectrum, and is similar to the shift

in the absorption band of phenol which occurs on the addition of
alkalies.   They state as a result of a reëxamination of the spectra
of these compounds:

We feel therefore that the chain of evidence against there being any
radical difference between the structure of the nitrophenols and their
sodium salts is completed by these observations and therefore are bound
to express ourselves against the quinoid configuration of the nitroanilines
and the sodium nitrophenoxides.

We have examined the absorption spectra of p-nitrophenol, o-
nitrophenol and p-nitrosophenol in absolute alcohol, and believe
that our evidence is conclusive in favor of the quinoid representa-
tion for these compounds in alkaline solution and that a chemical
equilibrum exists between the benzenoid and the quinoid forms
the position of which depends upon the concentration of the
alkali or acid.   When sufficient quantity of sodium ethoxide
is present in the alcohol solutions, the compounds are completely,
or almost completely, in the quinoid form, and in the presence
of a sufficient concentration of acid the reverse is the case.   Our
evidence on this point has been obtained by a simple method
which Baly and his coworkers have overlooked.

In the investigation of the phthaloximes [4] we were impressed
by the facts that in alkaline solution these compounds give a
color band which is entirely lacking in the absence of alkalies,
that this band falls in the region of the quinone color band, and
is, in many respects, identical with the color band of the nitro-
anilines, the salts of the nitrophenols, and of p-nitrosophenol;
and, moreover, the persistence of the color band, and consequent
depth of the color of the compound, depends exclusively, up to
certain limits, upon the concentration of the alkali.   Moreover,
no appreciable horizontal shift in the position of the head of the
band was observable with different concentrations of alkalies, the
effect of increasing concentration of alkali being merely to
increase the breadth and persistence of the band.   Believing that
the effect of alkalies was the production of a new form of
isorropesis which was not present in the original substance, we
were lead to the examination of nitrophenols and p-nitrosophenol
in an analogous manner, since Baly and his coworkers had
always employed, as we gathered from their papers, a concen-
tration of alkali equal to, or in excess of, that required to convert

[4] To appear.

Relative thickness of layer in millimeters of 1/10,000 molar solution.
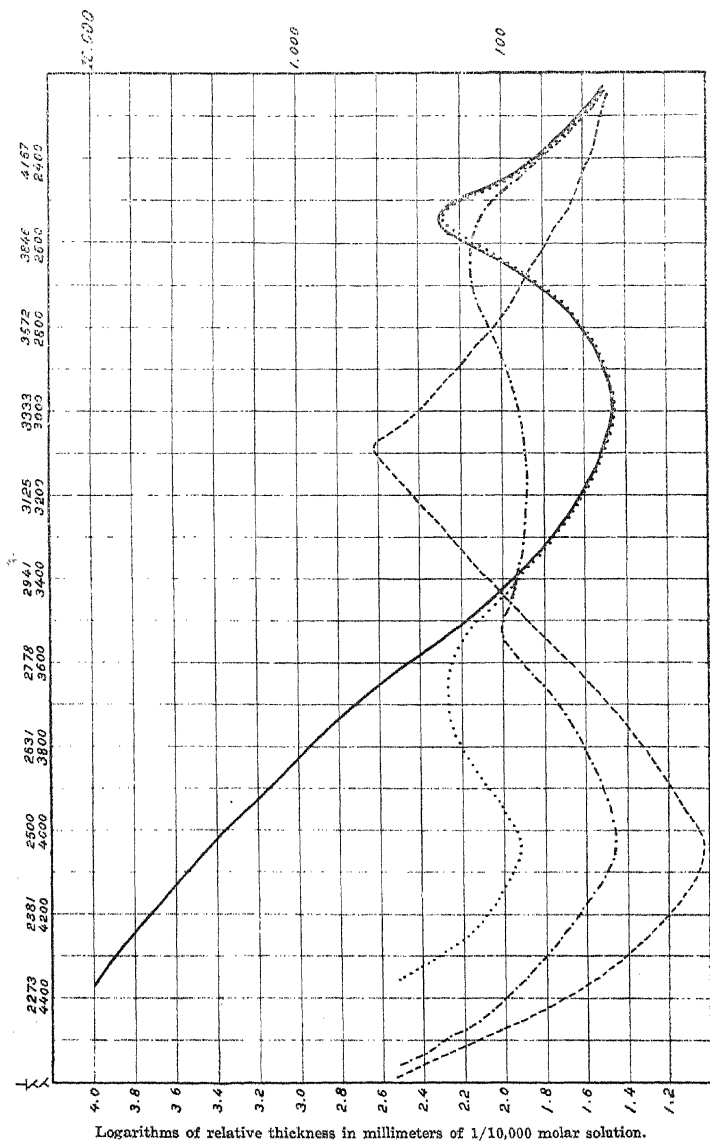
Logarithms of relative thickness in millimeters of 1/10,000 molar solution.

FIG. 1.—*P*-nitrophenol=full curve. *P*-nitrophenol with 1/10 equivalent of sodium ethoxide= dot curve. *P*-nitrophenol with ½ equivalent of sodium ethoxide=dot and dash curve. *P*-nitrophenol with 1 equivalent of sodium ethoxide=dash curve.

entirely the compound under investigation into the new form. Very conclusive results, which were more or less anticipated from a careful perusal of Baly's work, were obtained.

Four plates, somewhat typical of the many we have made, are reproduced full size at the end of this article in order to show the general character of the photographs from which our conclusions are drawn. Much detail present on the negative is lost in the reproductions which are therefore of little value for purposes of plotting curves. In the text figures the curves are plotted with the logarithms of the dilutions as ordinates and the wave lengths as abscissas. We employed the wave lengths rather than the oscillation frequencies for the reason that the region of the spectrum with which we are perhaps most concerned is thus more extended in the charts.

P-nitrophenol, by this method of investigation, is shown to have an absorption band, as described by Baly, Edwards, and Stewart,[5] heading at about 300 $\mu\mu$, which does not appreciably shift its position in the presence of alkalies. The shift of approximately 100 $\mu\mu$, which these authors show on the addition of alkalies, does not take place. What really happens is the formation of a new band heading at 405 $\mu\mu$. This band increases in persistence and breadth with the concentration of alkali, while the band heading at 300 $\mu\mu$ is correspondingly reduced in persistence. (Fig. 1.) When the molecular concentration of the alkali is equal to, or greater than, the concentration of the p-nitrophenol, the color band has reached approximately its maximum persistence and the band of the shorter wave length has entirely disappeared. This, in our minds, is capable of only one explanation and that is expressed by the chemical equilibrium:
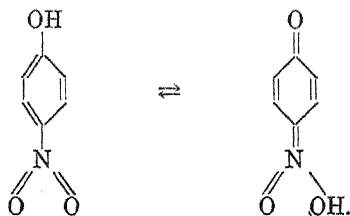
The band at 300 $\mu\mu$ is due to the benzenoid form while the color band at 405 $\mu\mu$ is produced by the salt of the quinoid form of the compound.

[5] *Ibid.*, fig. 6, p. 521.

Logarithms of relative thickness in millimeters of 1/10,000 molar solution.

Relative thickness of layer in millimeters of 1/10,000 molar solution.
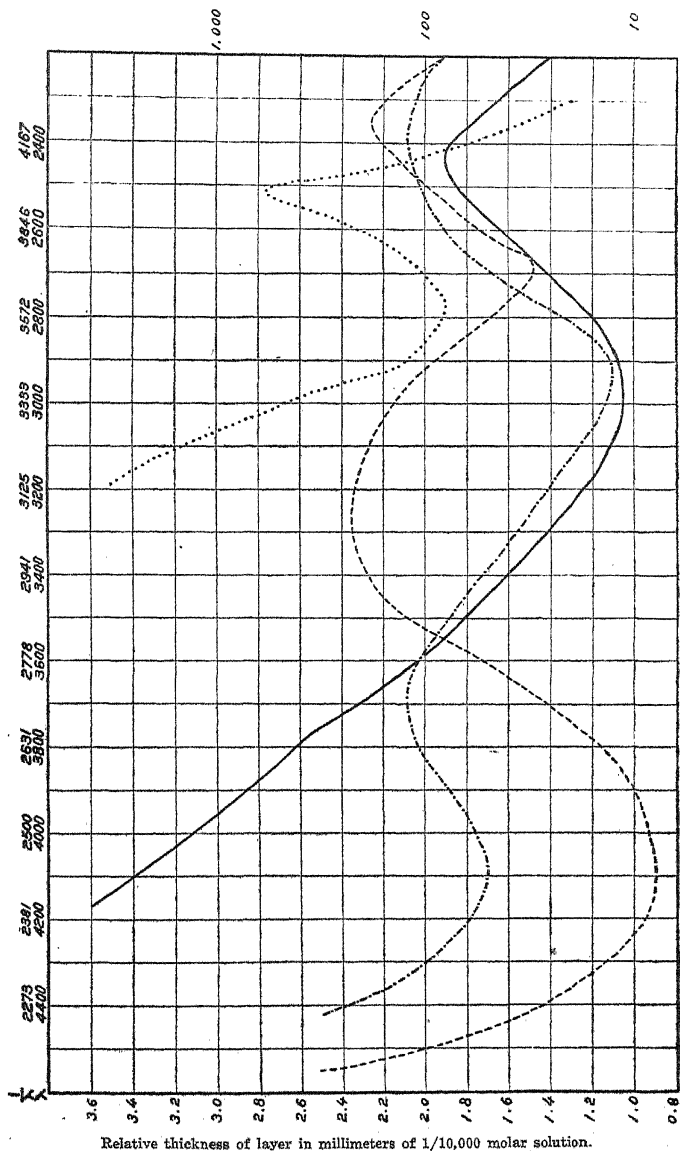
FIG. 2.—*P*-nitrosophenol=full curve. *P*-nitrosophenol saturated with HCl=dot curve. *P*-nitro-
sophenol with 1/10 equivalent of sodium ethoxide=dot and dash curve. *P*-nitro-
sophenol with 1 equivalent of sodium ethoxide=dash curve.

P-nitrosophenol in neutral, acid, and alkaline solutions shows equally striking results which are parallel in every respect to *p*-nitrophenol and indicate the chemical equilibrium which is customarily represented by the equation:

Our chart of the absorption curve of this compound (fig. 2) agrees with that of Baly, Edwards, and Stewart[6] and, had they photographed the compound in the presence of less than one equivalent of alkali it would have been evident that the band heading at 410 $\mu\mu$ is not due to a shift of over 110 $\mu\mu$ of the band heading about 300 $\mu\mu$, a shift in position which is in all probability impossible without a complete change in the character of the dynamic isomerism. In the presence of traces of hydrogen chloride, the general absorption in the visible spectrum is somewhat reduced while the remainder of the curve and the band heading at 300 $\mu\mu$ are not affected. The changes in the full curve (fig. 2) are so slight that the effect of traces of acid is not shown in the chart.

In *o*-nitrophenol[7] it is quite evident, from a study of the chart showing the curves of the absorption spectra (fig. 3), that the isorropesis is somewhat different from that found in the two preceding compounds and the band heading at 270 $\mu\mu$ is characteristic of this condition. The band heading at 345 $\mu\mu$ disappears progressively on the addition of alkalies, while a new band heading at about 420 $\mu\mu$ makes its appearance. The band at 270 $\mu\mu$ is also altered by the addition of alkalies, but to a much lesser degree than the other two bands. The curve of the absorption spectrum obtained with traces of hydrogen chloride is only slightly modified when the solution is saturated with this gas and it has been deemed unnecessary to plot this change upon the chart. The effect of high concentrations of hydrogen chloride is most apparent in the transmission band heading at 309 $\mu\mu$, the persist-

[6]*Ibid.*, fig. 7, p. 522.

[7]Armstrong [*Proc. Chem. Soc.*, London (1892), 101] suggested the quinoid formula for the o- and p-nitrophenols and proposed the name *quinone ortho nitroxime* for *o-nitrophenol*.

Logarithms of relative thickness in millimeters of 1/10,000 molar solution.
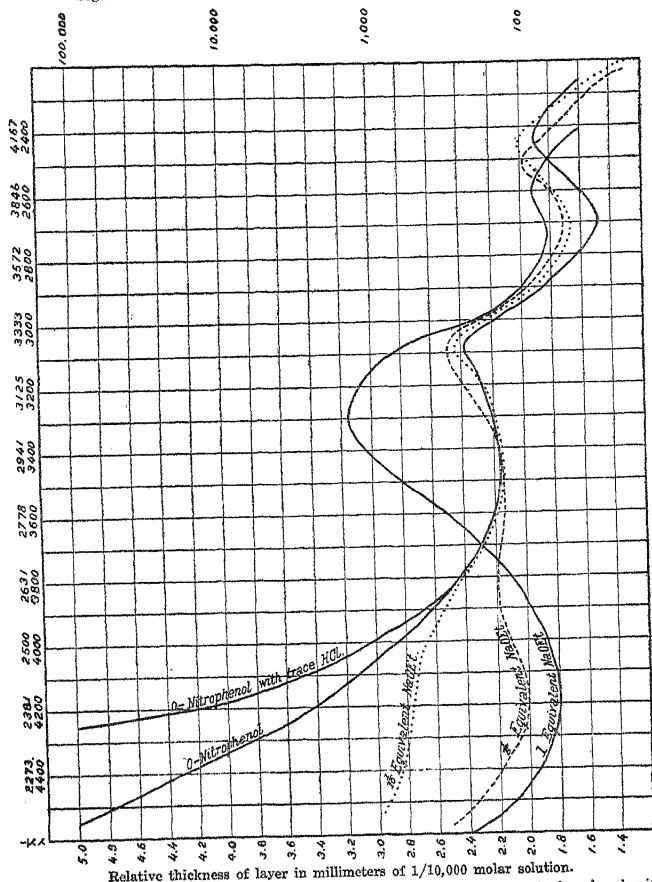
FIG. 3.—O-nitrophenol; O-nitrophenol with trace HCl=upper full curves. O-nitrophenol with 1/10 equivalent of sodium ethoxide=dot curve. O-nitrophenol with ⅔ equivalent of sodium ethoxide=dash curve. O-nitrophenol with 1 equivalent of sodium ethoxide= lower full curve.

ence of which is slightly reduced. The change in this compound is represented by the chemical equilibrium:
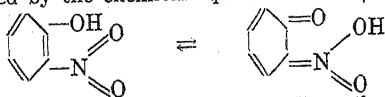
and from its behavior we are led to believe that there exists in it a greater inherent tendency for the transformation into

the colored modification than in either of the para compounds previously described.

Additional proof of the quinoid structure of the salts of *o*- and *p*-nitrophenol is found in the work of Baly, Edwards, and Stewart [8] which shows that the band heading at 300 $\mu\mu$ is present in *p*-nitroanisole and in its incipiency in *o*-nitroanisole, and that neither of these curves is altered in any way by the addition of alkalies. The fixation of the labile hydrogen atom in these cases, as in many others which could be cited, precludes the change to the quinoid form.

For purposes of comparison we have photographed phenol with various concentrations of alkali, and the small shift in the position of the band, about 20 $\mu\mu$, is of an entirely different character from that noted in the nitrophenols and *p*-nitrosophenol. The change in the band heading at 270 $\mu\mu$ on the addition of alkalies is not manifested by an increase in the persistence, but by a broadening of the band and a progressive movement toward the longer wave lengths. The extent of this movement depends upon the concentration of the alkali, but is not very great in the presence of a large excess of sodium ethoxide. Our plates check with the corresponding curves charted by Baly and Ewbank [9] and it does not seem necessary to plot the intermediate curves obtained with fractional equivalents of sodium ethoxide.

Baly, Tuck, and Marsden [10] have noted that all the nitro compounds containing the hydroxyl or amino groups in the ortho position give evidence of two bands, while the para isomerides show only one absorption band. They state:

The reason for this is not clear, but it seems to be characteristic of nearly all ortho disubstituted benzenes with two powerful groups of different types.

It seems to us that the generally accepted idea, that two groups para to each other are in closer relation than when in the ortho position, will, in some cases at least, have to be modified. Isorropesis appears to be more easily excited between the groups in the ortho than in the para positions. It is probable that at one stage of the vibration of the benzene ring the two groups para to each other may be in close proximity from which position they recede to a maximum distance in accordance with the expla-

[8] *Ibid.*, 518.
[9] *Ibid.* (1905), 87, 1351.
[10] *Ibid.*, 590.

nation of Baly, Edwards, and Stewart.[11] It is equally conceivable
that the groups in the ortho position may approach each other
to at least the same degree as in the para positions, while the
maximum of their separation is less than that possible in the
latter case.   The average of the influence of the two substituted
groups upon each other might be much greater when they are
in the ortho positions.

We are convinced that a reëxamination of the absorption
spectra of some of the compounds, which Baly, Tuck, and Mars-
den [12] cite to oppose the quinoid theory, will show that the
great shift in the position of a band on the addition of alkali
is impossible and that the apparent shift is really the destruction
of one band and the formation of a new one, a process which
takes place progressively as the concentration of the alkali
is increased.

Hantzsch and Voigt [13] in discussing the relations existing be-
tween p-nitrophenol and nitrobarbituric acid,

$$HO\langle\rangle NO_2 \qquad\qquad O{=}C\langle\genfrac{}{}{0pt}{}{NH{-}CO}{NH{-}CO}\rangle CH. NO_2$$
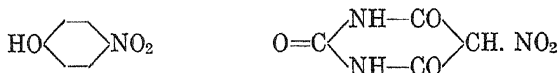
have assumed that the great change in the absorption spectrum
of the former and slight alteration that takes place in that of the
latter in the presence of alkali did not vitiate the exact analogy
between the two substances.   The evidence that the band of
p-nitrophenol salts is an entirely new band from that shown
by p-nitrophenol itself, while the band of nitrobarbituric acid
is actually shifted by alkali, would indicate that the benzene ring
plays an important part in *aci-conjugated* nitro compounds rather
than an unimportant rôle as these authors state; and that their
analogy between these two compounds is therefore not justified.

Since writing this article we have received the September
issue of the Journal of the Chemical Society (London) and note
the article by Hewitt, Pope, and Willett.[14]   From their descrip-
tion of the absorption spectra of p-nitrophenylacetonitrile and
some related compounds, it is evident that the structure of these
substances in alkaline solution is capable of the same explanation
as that applied to nitrophenols.

[11] *Ibid.*, 524.

[12] *Ibid.* (1910), **97**, 571 and 1494.

[13] *Ber. d. deutschen chem. Ges.* (1912), **45**, 103.

[14] The absorption spectra of nitro compounds, *Journ. Chem. Soc. London*
(1912), **101**, 1770.

SUMMARY.

In this paper new evidence is introduced to show that the benzenoid configuration represents the structure of the *o*- and *p*-nitrophenols and *p*-nitrosophenol in neutral and acid alcohol solutions, and the quinoid configuration that of the salts in solutions in alcohol.

The addition of fractional equivalents of sodium ethoxide to the neutral solutions of these compounds produces a new absorption band in the visible region of the spectrum. This band increases progressively in breadth and persistence with increasing concentrations of alkali and is a measure of the transformation of the benzenoid to the quinoid form.

Baly, Edwards, and Stewart originally believed that these compounds in alkaline solution were best represented by the quinoid structure. Baly, Tuck, and Marsden, four years later, contradicted the first article and advanced a different theory to explain the color of the salts. We believe that the latter authors have evolved a false theory from their experimental data.

ILLUSTRATIONS.

TEXT FIGURES.

PLATE I. O-NITROPHENOL WITH ONE-FIFTH EQUIVALENT OF SODIUM ETHOXIDE. 1/1000 MOLAR SOLUTION. THICKNESS OF LAYER, 32 TO 2 MILLIMETERS.

PLATE II. O-NITROPHENOL WITH 1 EQUIVALENT OF SODIUM ETHOXIDE. 1/1000 MOLAR SOLUTION. THICKNESS OF LAYER, 32 TO 2 MILLIMETERS.

PLATE III.   P-NITROSOPHENOL WITH 1 EQUIVALENT OF SODIUM ETHOXIDE.   1/1000 MOLAR SOLUTION.   THICKNESS OF LAYER, 32 TO 2 MILLIMETERS.
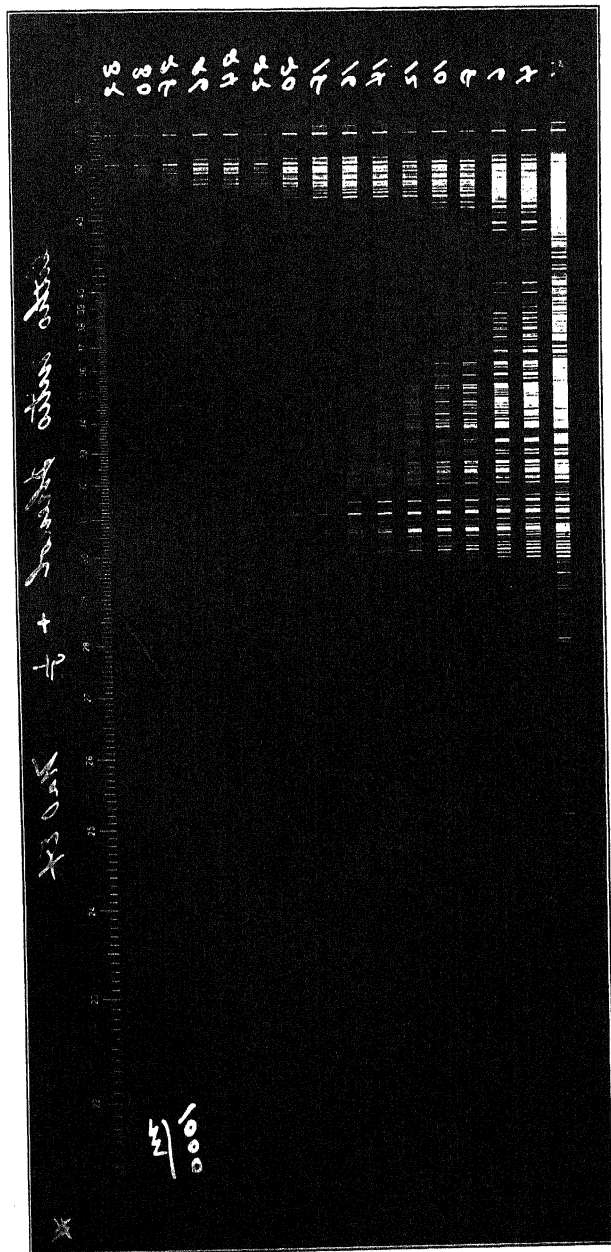
PLATE IV. P-NITROPHENOL WITH ONE-TENTH EQUIVALENT SODIUM ETHOXIDE. 1/1000 MOLAR SOLUTION. THICKNESS OF LAYER, 32 TO 2 MILLIMETERS.

SOME FILIPINO FOODS.

By H. D. Gibbs[1] and F. Agcaoili.

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With the coöperation of

G. R. Shilling.[2]

(*From the Bureau of Health, Manila, P. I.*)

CONTENTS.

INTRODUCTION.

The people of almost every country of the world are accustomed to certain foods which are ignored or ridiculed by the people of other nations. Many of these foods, which are considered delicacies by some, are regarded with disgust by others. We have collected some data on this subject in the Philippine Islands, and present the results in this paper.

Dampier, who visited the Batan Islands, now Batanes Province, in 1687, describes[3] some peculiar dishes of which the natives were very fond.

I did never see them kill any of their Goats or Hogs for themselves, yet they would beg the Paunches of the Goats that they themselves did sell to us; And if any of our surly Seamen did heave them into the Sea, they would take them up again and the Skins of the Goats also. They would not meddle with Hogs-guts, if our Men threw away any besides what they made Chitterlings and Sausages of. The Goat-skins these People would carry ashore, and making a Fire they would singe off all the Hair, and afterwards let the Skin lie and parch on the Coals, till

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[1] Associate professor of chemistry, University of the Philippines.
[2] Food and drug inspector, Bureau of Health.
[3] Dampier's Voyages. London (1906), 1, 423.

they thought it eatable; and then they would gnaw it, and tear it in pieces with their Teeth, and at last swallow it. The Paunches of the Goats would make them an excellent Dish; they·drest it in this manner. They would turn out all the chopt Grass and Crudities found in the Maw into their Pots, and set it over the Fire, and stir it about often: This would Smoak and Puff, and heave up as it was Boyling; wind breaking out of the Ferment, and making a very savory Stink. While this was doing, if they had any Fish, as commonly they had 2 or 3 small Fish, these they would make very clean (as hating Nastines belike) and cut the Flesh from the Bone, and then mince the Flesh as small as possibly they could, and when that in the Pot was well boiled, they would take it up, and strewing a little Salt into it, they would eat it, mixt with their raw minced Flesh. The Dung in the Maw would look like so much boil'd Herbs min'd very small; and they took up their Mess with their Fingers, as the Moors do their Pillaw, using no Spoons.

They had another Dish made of a sort of Locusts, whose bodies were about an Inch and an half long, and as thick ɛs the top of one's little Finger; with large thin Wings, and long and small Legs. At this time of the Year these Creatures came in great Swarms to devour their Potato-leaves, and other Herbs; and the Natives would go out with small Nets, and take a Quart at one sweep. When they had enough, they would carry them home, and parch them over the Fire in an earthen Pan; and then their Wings and Legs would fall off, and their Heads and Backs would turn red like boil'd Shrimps, being before brownish. Their Bodies being full, would eat very moist, their Heads would crakle in one's Teeth. I did once eat of this Dish, and liked it well enough; but their other Dish my Stomach would not take.

In various parts of the Islands locusts, beetles and their larvæ, bees, crickets, snails, snakes (principally the python), lizards (principally the iguana), and other animals are eaten, and some of these are highly regarded as delicacies. The list of insects which are most commonly eaten, with their native names, has been furnished us by W. Schultze, of the Bureau of Science.

The order Coleoptera, or beetles, includes: *Oryctes rhinoceros* Linn., *u-ang* (Tagalog); *Rhynchophorus ferrugineus* Oliv., *u-ang* (Tagalog); and *Batocera numitor* Newm., *u-ok* (Tagalog), the larvæ only of which are eaten. Of *Hydrous picicornis* Chevr., *ubus* (Visayan), *alukap* (Ilocano); *Lepidiota punctum* Blanch., *sibung* (Tagalog); *Leucopholis irrorata* Chevr.; and *Leucopholis pulverulenta* Burm., *salagubang* (Tagalog), the adults only are eaten, either boiled or roasted after the wings and legs have been removed.

The order Orthoptera includes: *Locusta danica* Linn., *Acrydium rubescens* Stoll., *Acrydium ranunculum* Walk., *Curtilla africana* Bea., *sosohong* (Tagalog), and some other related species, the larvæ and adults of which are eaten, usually fried.

The native name for the young is *lukton* (Tagalog) and for the adults, *balang* (Tagalog).

The order Hymenoptera includes: *Megapis* (*Apis*) *zonata* Smith, *Megapis* (*Apis*) *dorsata* Fabr., *pukyutan* (Tagalog), and *Apis indica* Fabr., *leyuan* (Tagalog), all being bees, the honey and also the comb containing larvæ of which are eaten.

At the time of the beginning of the enforcement of the Food and Drugs law, Act No. 1655 of the Philippine Commission, May 18, 1907, a study of native food and drinks was commenced.[4] We have been handicapped in this work owing to the difficulties encountered in obtaining reliable information from the various parts of the Islands without personal exploration, the value of which, in many cases, is not commensurate with the labor and expense. The manufacture of food products in the provinces is at a minimum, and is in almost all cases, except the alcohol and sugar industries, only for local consumption. In Manila the manufacture of a few foods is carried on in a small way.

BAGOONG.

Bagoong is a mixture of small fish and salt which has undergone a process of fermentation. Artificial coloring is sometimes added. This food product is known throughout the Philippine Islands under different names according to the dialects spoken, and probably there are no markets without a place where bagoong of different kinds is sold on a small scale. Most of the products which are put on the markets in Manila come from the provinces where they are made in large quantities. In many towns, if not all, especially in the north, bagoong is one of the principal foods of the people. In fact, most families of the poorer class can live very comfortably on bagoong and boiled rice alone. Its manufacture is carried on entirely by the natives, and the process requires only a *bolo*[5] to cut the larger fishes into small pieces.

[4] The investigations so far as published include: Editorial: Food and drug inspection. *This Journal, Sec. A* (1908), 3, 44; On the detection and determination of coconut oil, *ibid.*, 371; Editorial: Proprietary medicines in the Orient, *ibid.*, 411; The alcohol industry of the Philippine Islands, Part I. A study of some palms of commercial importance with special reference to the saps and their uses, *ibid.* (1911), 6, 99 to 206; Part II. Distilled beverages, their consumption and manufacture, *ibid.* (1912), 7, 19; Part III. Fermented beverages which are not distilled, *ibid.*, 97; Soja-bean curd, an important oriental food product, *ibid.*, 47. Several other articles on food products are in preparation.

[5] A heavy, long-bladed knife used by the natives.

The coloring substances employed are termed *ankak* and *grana* (Tagalog). The former is prepared by soaking rice in solutions of certain wood dyes and then drying. The dried red rice is powdered and used in quantities to produce the desired tint. The latter is cochineal.

There is no doubt that this class of food substances is a violation of the Food and Drugs Act, for it "consists wholly or in part of a filthy, decomposed, or putrid animal substance," and in many cases is dangerous to health. Since this food is only eaten by natives, the enforcement of the law would be extremely difficult and unpopular and has not been attempted as yet.

Bagooñg, bog-go-oñg as it is called in the Ilocano provinces, where it is manufactured in greater variety and probably in larger quantity than in any other province, is composed of many kinds of small salt-water fishes. Among the varieties commonly employed are the anchovy [*Anchovia commersoniana* (Lacépède)], called by the Moros *anakbat,* by the Ilocanos *monamon,* and by the Tagalogs *dilis;* the slip mouth [*Leiognathus splendens* (Cuv.)], termed quite generally by the natives *sapsap;* and young of various species of herring (*Harengula*), designated by the Moros *pinatai,* by the Ilocanos *bilis,* and by the Tagalogs *siliñasi;*[6] and also the young of the Siganidæ.

The fish are put into a large basket, washed and drained, and then mixed with salt varying in proportion from 1 part salt and 2 parts fish to 2 parts salt and 3 parts fish. The mixture is put in earthen jars called *burnai* and covered with banana leaves and clay. After three months the bagooñg is ready for sale. The odor, flavor, and selling qualities improve with age. Experts can estimate approximately the age of the food by the odor, and many claim that the more putrid and disagreeable the odor, the better is the flavor. It is eaten raw or fried, but is more desired as a condiment to other viands.

TABLE I.—*Analysis of bagooñg.*

Constituent.	Per cent.
Solids	42.30
Water	57.70
Protein ($N \times 6.25$)	13.44
Fat	1.25
Ash	24.98
Sodium chloride	22.04

[6] A number of the fishes of the Philippine waters are described by Alvin Seale, *This Journal, Sec. A* (1908), 3, 513.

Another method of manufacturing bagooñg found to be in use in Cavite is as follows:

Small fish, the young of the *dilis,* are mixed with an equal amount of salt and allowed to stand four or five days or until the salt is entirely liquefied. The liquid is then poured off and replaced with ankak (red rice) solution to which a small quantity of wine has been added to improve the aroma and flavor. Nipa [7] wine or *anisado* [8] is employed for this purpose. After five or six days the bagooñg is ready for consumption either raw or fried. Lemons, or *calamansi* (*Citrus mitis* Blanco), are sometimes mixed with the food in place of the wine. This bagooñg has the appearance of small fishes swimming in red wine.

The liquid portion was decanted from the solid and the two portions analyzed separately.

TABLE II.—*Analysis of bagooñg.*

Constituent.	Liquid. Per cent.	Solid. Per cent.
Solids	24.30	31.62
Loss at 100° C.	75.70	68.38
Protein ($N \times 6.25$)	7.50	10.14
Fat	0.68	3.53
Ash	15.34	15.60
Sodium chloride	12.36	12.40
Alcohol	4.02	——

BAGOOÑG ALAMAÑG.

Another variety of bagooñg, which is known by the name of *bagooñg alamañg,* is made of 4 parts of *alamañg* (small shrimps) and 1 part of salt. After the shrimps are washed and drained, the necessary amount of salt is thoroughly mixed with the crustaceans. The mixture is kept in jars for at least a month before it is ready for sale. This food can be kept for years without spoiling. Sometimes, however, vendors manufacture it on a very small scale, employing less salt, so that after fifteen days it becomes black; the odor is then unbearable and should be designated as a stench.

TABLE III.—*Analysis of bagooñg alamañg.*

Constituent.	Per cent.
Solids	32.13
Water	67.87
Protein ($N \times 6.25$)	15.68
Fat	2.22
Ash	14.30
Sodium chloride	11.77

[7] Wine made by fermenting the juice of the nipa palm.
[8] Anisette cordial.

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This food is sold with or without the addition of artificial color.

Two by-products of bagooñg alamañg are termed *patis* and *he-ko*. They are obtained by squeezing the bagooñg with the hands, taking a handful at a time. The solid portion thus obtained is colored with either grana or ankak to improve the looks of the pressed material, and salt added until the taste resembles the original. It is sold on the market as bagooñg alamañg. This imitation spoils in about five days.

TABLE IV.—*Analysis of pressed alamañg.*

Constituent.	Per cent.
Total solids	30.92
Water	69.08
Protein	10.44
Fat	1.15
Ash	15.20
Sodium chloride	14.42

The liquid portion which is obtained on squeezing the bagooñg alamañg is boiled for half an hour and left to stand until precipitation is complete. The clear, supernatant liquid is decanted and bottled. This is the so-called *patis,* a favorite sauce or condiment of the natives, and is used for almost every kind of viand.

TABLE V.—*Analysis of patis.*

Constituent.	Per cent.
Solids	32.15
Water	67.85
Protein	4.51
Fat	3.27
Ash	23.04
Sodium chloride	22.72

The precipitate, called he-ko, answers all the purposes for which any kind of bagooñg is used and is a condiment for salads and boiled vegetables.

TABLE VI.—*Analysis of he-ko.*

Constituent.	Per cent.
Total solids	35.63
Water	64.37
Protein	12.38
Fat	0.90
Ash	20.70
Sodium chloride	18.71

Besides the bagooñg mentioned above, there are other varieties which are made practically in the same way, although of different materials. Examples of these are: *bagooñg amled*, a compound of salt and *amled*, a fish of the family Gobiidæ; *bagooñg padas*, the compound of salt with young fish (*Siganus*) of the family Siganidæ. The name of this food, *padas*, was given to it by the natives in the north by a mere accident. The word padas (Ilocano) (*kuijug* in Camarines) means to try. A fisherman caught many of these fish one day and, out of curiosity, tried to manufacture them into bagooñg. To his surprise he found that these fish were better material than any other kind used in the manufacture. *Bagooñg ipon* is made from the young of the family Gobiidæ. These are sea fish, about 3 centimeters long and a few millimeters thick, and are caught by the ton. Other kinds of bagooñg of less importance are *birabid* and *bagis*. The former is made of a certain kind of mollusk which is found in stagnant portions of rivers, and the latter of the intestines of large fish, among which is the *bañgos*, or milk fish [*Chanos chanos* (Forskål)].

Very recently a bagooñg has been produced by the Ilocanos from tomatoes. It is made in the same way as when fish are employed and is called *bagooñg á camatis*.

DRIED FISH.

Small-sized fishes are dried quite generally throughout the Philippine Islands and sold under various native names descriptive of the process of preparation or of the variety of fish employed. The methods employed are very simple. The fishes are spread upon trays, or often on the sandy beach, and exposed to the sun for about one day. (Plate I, fig. 1.) Sometimes they are salted during the process, or boiled in salt water previous to the drying, and sometimes smoked over a wood smudge. In and around Manila saw-dust fires are employed. (Plate I, fig. 2.)

Daing (Ilocano) is sun-dried fish of various kinds. *Tuyu* (Tagalog, dried) is prepared by washing the fishes and then soaking them in a strong brine for from one to six hours after which they are spread on bamboo frames and dried in the sun for one or two days. *Tinapa* (Tagalog) is prepared by smoking fish over burning rice husks or saw dust. The fishes are washed with boiling water, and, for some varieties, with vinegar. The smoking is done over an earthen oven, the smoke issuing from a hole in the top over which tiers of bamboo baskets containing

the fish are placed. Eight or ten baskets are placed one above the other and the smoke passes through all. The baskets are continually shifted from the bottom to the top at about five-minute intervals, and at the end of each circuit the fishes are turned over.

The species of fishes usually employed are *Anchovia commersoniana* (Lacépède), anchovy (English), *dilis* (Tagalog); *Leiognathus splendens* (Cuv.), slip mouth (English), *sapsap* (Tagalog); the young of *Harengula moluccensis* Bleeker, *H. gibbosa* Bleeker, herring (English), *siliñasi* (Tagalog), *aber* (Ilocano); family Trichiuridæ, band fish (English), *espada* (Spanish), *bolong onas* (Ilocano); family Hæmulidæ, grunt family (English), *bakuku* (Tagalog); and others.

Dilis are usually washed and dried in the sun for about two days. Sapsap and espada are usually prepared and sold as tuyu. Siliñasi are usually made into tinapa.

Analyses of various samples obtained in and around Manila are as follows:

TABLE VII.—*Analyses of dried fish.*

Character of sample.	Number of fish examined.	Total weight.	Weight of each fish.	Solids.	Fat.	Protein (N×6. 25).	Ash.	Sodium chloride in ash.	Remarks.
		Grms	*Grms.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	
Bakuku and sapsap	16	101	6.35	68.57	5.74	35.00	26.76	12.08	The high ash is caused by sea sand and by the bony character of the fish.
Dilis	57	35	0.62	74.71	6.52	35.90	29.42	1.24	Ash contains much sand from drying the fish on the beach.
Espada	3	152	50.67	62.04	4.28	33.69	23.53	15.21	Do.
Tinapa	7	88	12.57	43.98	4.87	28.00	10.18	3.92	Smoked fish.
Tuyu	6	57	9.50	55.10	7.57	30.63	16.24	12.40	Sun-dried fish.

BALUT.

The Tagalog word *balut* means to wrap into a bundle and it also refers to a half-hatched egg. The connection between the two is explained by the idea that the half-developed chick is still enclosed in a membrane or wrapped in a bundle.[9] In various

[9] We are indebted to Mr. Epifanio Santos, treasurer of the Province of Bulacan, for much information.

parts of the Islands the food product balut is manufactured from ducks' and hens' eggs. The half-hatched eggs are considered a delicacy and retail in and around Pateros for from 4 to 6 centavos each, and at this time the wholesale price is 30 pesos per thousand.

The industry is highly developed in the Provinces of Rizal and Laguna, where only ducks' eggs are employed. On the Islands of Negros and Panay some balut is made from ducks' and hens' eggs, and in other places, no doubt, the manufacture is carried on to a limited extent. The center of trade is the town of Pateros on the Pasig River in the Province of Rizal. The town has derived its name from the industry, *patero* (Spanish) meaning a person who takes care of ducks. Here the magnitude of the business depends almost entirely on the supply of ducks' eggs. In addition to the eggs originating in the immediate locality, large numbers are shipped from a distance, and after being made into balut are reshipped to an extensive surrounding territory. Exact figures concerning the extent of the industry are not readily obtainable, but some idea of its magnitude is shown from the fact that one building in Pateros, the largest engaged in the business, has a capacity of 80,000 eggs hatching at one time.

The reasons for the employment of ducks' eggs almost to the exclusion of hens' eggs are purely economic. Fresh ducks' eggs are very cheap and of little value, but when made into balut are highly prized by the natives, while fresh hens' eggs are comparatively scarce and command a high price. The expense of keeping ducks, according to the native method, is very low, and requires only a house and a corral. (Plate II, fig. 1.) Under these conditions the ducks will find their own food and are practically no expense. On the other hand, hens require more care and feeding.

The process of manufacture is very simple and, after the eggs are laid, quite independent of the ducks, which in this locality usually will not hatch the eggs. The heat necessary for the incubation is obtained by warming the rice, in which the eggs are packed, for a few seconds in a kettel over a fire each time the eggs are tended. The eggs are packed in bamboo cylinders, 50 centimeters in diameter by 80 centimeters in length, which rest upon a layer of rice husks about 10 centimeters deep upon the earthen floor of the building. Alternate layers of warm unhusked rice, called *palay* (Spanish), and eggs fill the cylinder. There are usually 8 layers of about 125 eggs each, thus making

about 1,000 to the receptacle. The top is usually covered with an empty sack and a layer of rice husks. The bamboo cylinders containing the eggs are surrounded by rice husks. Twice each day at 6 o'clock in the morning and 5 o'clock in the afternoon the eggs are repacked, probably for the purpose of turning them over and also to allow the entrance of air and heating the rice. Plate II, fig. 2, illustrates this form of incubator. After eighteen days of incubation, the eggs are boiled in water and sold as balut.

Large numbers of ducks are hatched in a slightly modified form of the same apparatus. When it is desired to carry the incubation process to completion, the balut stage is first carried on as described, after which more care is used and only single layers of eggs are packed in the unhulled rice. The eggs are not completely buried in the rice, but are covered with sacking and a thick layer of rice hulls, and in this case the turning and repacking process is carried on three times each day, every four hours during the daytime. The eggs hatch in about thirty-three days. The operation of turning the eggs is illustrated in Plate III, fig. 1.

A household industry of making balut and hatching the eggs by means of the heat of the human body was formerly more extensively engaged in than at present. The eggs were put in racks under the chairs, or under beds and sometimes in belts which were fastened around the waist. The health officials have been instrumental in discouraging these practises.

König [10] gives the constituent of hen's and duck's eggs as follows:

TABLE VIII.—*Weight and percentage of yolk albumen, and shell in hen's and duck's eggs.*

Constituent.	Hen's egg.		Duck's egg.	
	Grams.	Average per cent.	Grams.	Per cent.
Weight of one egg	30 to 72		60	
Yolk	10 to 23	30.0	24	40
Albumen	15 to 43	58.5	30	50
Shell	3 to 7	11.5	6	10

[10] Chemie der menschlichen Nahrungs- und Genussmittel. Berlin (1904), 2, 573. See also 1, 99 and 1471.

TABLE IX.—*Analyses of hen's and duck's eggs.*

Constituent.	Hen's egg.	Duck's egg.
	Per cent.	Per cent.
Composition of the whole egg:		
Shell	11.40	13.30
Water	73.67	70.81
Nitrogenous substances	12.57	12.77
Fat	12.02	15.04
Nitrogen-free extract	0.67	0.30
Ash	1.07	1.08
Composition of the albumen:		
Water	85.61	87.00
Nitrogenous substance	12.77	11.10
Fat	0.25	0.03
Nitrogenous-free extract	0.70	1.07
Ash	0.67	0.80
Composition of the yolk:		
Water	50.93	45.80
Nitrogenous substance	16.05	16.00
Fat	31.70	36.20
Nitrogen-free extract	0.29	....
Ash	1.02	1.20

The compounds found in the yolk and albumen of hen's eggs are summarized by Simon,[11] and the results given below vary only slightly from those stated by König.

TABLE X.—*Hen's egg. Composition of the yolk.*

Constituent.	Per cent.
Water	47.19 to 51.49
Solids	48.51 to 42.81
Fat (olein, palmitin, and stearin)	21.30 to 22.84
Vitellin and other albumins	15.63 to 15.76
Lecithins	8.43 to 10.72
Cholesterin	0.44 to 1.75
Cerebrin	0.30
Mineral salts	3.33 to 0.36
Coloring matter } Glucose	0.553
Reaction feebly alkaline.	

[11] A text-book of Physiological Chemistry. Philadelphia and New York (1904), 456–460.

TABLE XI.—*Hen's egg. Composition of the ash of the yolk.*

Constituent.	Per cent.
Sodium (Na_2O)	5.12 to 6.57
Potassium (K_2O)	8.05 to 8.93
Calcium (CaO)	12.21 to 13.28
Magnesium (MgO)	2.07 to 2.11
Iron (Fe_2O_3)	5.72
Phosphoric acid, free (P_2O_5),	1.19 to 1.45
Phosphoric acid, combined,	63.81 to 66.70
Silicic acid (SiO_2)	0.55 to 1.40
Chlorine	trace

TABLE XII.—*Hen's egg. Composition of the albumen.*

Density	1.045
Reaction	alkaline

Constituent.	Per cent.
Water	80.00 to 86.68
Solids	13.32 to 20.00
Albumins	11.50 to 12.27
Extractives	0.38 to 0.77
Glucose	0.10 to 0.50
Fats and soaps	traces
Mineral salts	0.30 to 0.66
Lecithins and cholesterin	traces

TABLE XIII.—*Hen's egg. Composition of the ash of the albumen.*

Constituent.	Per cent.
Sodium (Na_2O)	23.56 to 32.93
Potassium (K_2O)	27.66 to 28.45
Calcium (CaO)	1.74 to 2.90
Magnesium (MgO)	1.60 to 3.17
Iron (Fe_2O_3)	0.44 to 0.55
Chlorine (Cl)	23.84 to 28.56
Phosphoric acid (P_2O_5)	3.16 to 4.83
Carbonic acid (CO_2)	9.67 to 11.60
Sulphuric acid (SO_3)	1.32 to 2.63
Silicic acid (SiO_2)	0.28 to 0.49
Flourine (F)	trace

TABLE XIV.—*Our analyses of fresh and hard-boiled ducks' eggs and cooked and uncooked balut.*

Kind of egg.	Weight of—			Water (loss at 100°).	Ni-trogen-ous sub-stance.	Fat.	Ash.	Total.
	Egg.	Shell.	Edible portion.					
	Grams.	*Grams.*	*Grams.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Hard-boiled egg	61.8	9.2	52.6	71.36	13.59	14.12	1.03	100.10
Fresh egg	64.0	9.1	54.9	72.88	13.04	13.92	0.98	100.82
Cooked balut	70.0	10.0	60.0	70.40	15.63	12.84	0.97	99.84
Uncooked balut	69.34	6.67	62.67	71.76	12.69	14.23	0.99	99.67

It is seen from the above analyses that the changes taking place during the eighteen days of incubation only slightly affect the relationship between the fats and the nitrogenous compounds. These two classes of compounds are represented by many members, and the yolk and albumen of the egg contain all the elements necessary for the growth of the embryo. Very little is known concerning the series of chemical changes that go on in them during incubation. It is generally stated that the eggs lose weight, chiefly due to loss of water; the solids, especially the fats and proteids, decrease; carbon dioxide, nitrogen, or nitrogenous substances are given off; and a respiratory exchange of gases takes place.[12]

Liebermann,[13] who has studied the subject most carefully, gives the following interesting table showing the increase in hæmoglobin, a compound practically absent in the egg.

TABLE XV.—*Increase in hæmoglobin in the egg during incubation.*

Duration of incubation.	Weight of embryo.	Hæmo-globin.	Hæmo-globin.	Hæmo-globin in relation to body weight.
Days.	*Grams.*	*Grams.*	*Per cent.*	
11	3.569	0.0049	0.14	1:728
14	8.175	0.0155	0.19	1:527
14	9.358	0.0131	0.14	1:714
15	10.958	0.0284	0.26	1:385
21	26.198	0.0384	0.23	1:421
8-day-old chick	35.600	0.1687	0.47	1:211

Since the blood is stated to be 8.2 per cent hæmoglobin, the increase can be approximately calculated from the above figures. The approximation shows that balut contains 0.5-per-cent blood.

The changes which take place in the egg upon storage [14] are naturally quite different from those occurring in the egg during incubation. In the former case the organic (lecithin) phosphorus undergoes a process of change to inorganic compounds, the coagulable proteid decreases, while the proteoses and peptone nitrogen increases, and apparently the amido compounds show a tendency to decrease.

[12] Hammarsten, Mandel, Text-book of Physiological Chemistry. New York (1904), 435.

[13] *Arch. f. d. gesamm. Physiol.* (1888), 43, 139.

[14] H. W. Wiley *et al.*, A preliminary study of the effects of cold-storage on eggs, quail, and chickens, *Bull. U. S. Dept. Agr., Bur. Chem.* (1908), 115.

Concerning the nutritive value of balut it can be said that there is little change from the calorific value of the fresh egg, and it seems probable that the digestibility is only slightly altered.

LOCUSTS.

Locusts occasionally devastate sections of the Philippine Islands, leaving nothing for the grazing animals which often die for lack of food. Some tribes highly prize these insects as articles of food, while other inhabitants do not eat them at all.

Locusts occur throughout the Philippines, and sometimes the numbers assume astonishing proportions. A severe outbreak of these pests is now (September, 1912) at its height in the Islands of Cebu, Leyte, Bohol, Samar, Negros, Masbate, and northern Mindanao, and much damage is being done to agricultural interests.

TABLE XVI.—*Analysis of 300 locusts (genus Acrydium).*

	Grams.
Total weight	500.00
Average weight of each locust	1.67
Edible portion, body and head	405.00
Waste, legs, and wings	95.00

Constituent.	Per cent.
Edible portion (percentage of whole)	81.00
Total solids	40.39
Moisture (loss at 100°)	59.61

Protein (N × 6.25)	24.13
Fat	7.89
Ash	1.79
Undetermined	6.58
	40.39

BIHON, MISUA, AND MIQUE.

The Chinese in Manila make from flour several food products which resemble vermicelli, macaroni, and similar foreign foods. The places of manufacture, numbering about 12 in Manila, are all small and the apparatus crude. The business is usually owned by a Chinaman who employs as laborers a few of his countrymen and some Filipinos, and lives with his workmen and family in the same building, often in the same room where the food product is prepared. The best known of these foods are used quite generally throughout China, and in Manila are called by the Chinese names *bihon, misua,* and *mique.* A number of factories have been investigated and samples obtained and

analyzed. The details of the process of manufacture may differ slightly in different establishments, but the essentials are the same.

Bihon.—This product is made from milled rice and resembles macaroni. The rice is first washed and then soaked overnight in water, ground between millstones to a finely divided liquid suspension, and run into linen bags or old flour sacks. (Plate III, fig. 2.) After standing about twenty-four hours, much of the water drains from the sacks, the contents become firmer, and shrink about 25 per cent in volume. The rice is then kneaded by hand, or pounded in a wooden mortar with wooden hammers until homogeneous, and then patted into balls which are boiled in water for about one hour. They are then pressed through round holes in the bottom of a metallic box, thus producing strings which are about three times as thick as vermicelli. (Plate IV fig. 1.) These are again boiled for about an hour and then laid on bamboo frames, in flat boxes 15 or 20 centimeters square, and placed in the sun to dry. A day is sufficient for drying, after which they are ready for market.

Misua.—This food product resembles vermicelli and is made from wheat flour. The dough, made by mixing salt water and flour, is rolled into small ropes and then stretched into long thin strings which are hung in the sun to dry. A flour imported from China and also made locally from the sweet potato (*Ipomoea batatas* Poir.), locally known as camote, is often used on the mixing boards when the dough is kneaded but is not incorporated in the mixture to any great extent. (Plate IV, fig. 2, and Plate V, fig. 1.)

Mique.—This product is made from wheat flour in much the same manner as misua. The dough is made with saline water to which a small quantity of alkali is added, principally for the purpose of making the food a golden yellow. The alkali is usually obtained by leaching wood ashes or the ashes of tobacco stems, and the solution is used for mixing the dough. The dough is cut into strings about 20 centimeters long, boiled for two or three hours, and dried in the sun. (Plate IV, fig. 2, and Plate V, fig. 1.)

Analyses of these three foods are given in the following table, together with analyses of macaroni, vermicelli, rice, and wheat [16] for purposes of comparison.

[16] Leach, Food Inspection and Analysis. New York (1905), 212 and 263.

TABLE XVII.—*Analyses of native products resembling vermicelli and macaroni.*

Determination.	Mique.	Misua.	Bihon.	Maca-roni.	Vermi-celli.	Rice.	Wheat.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Moisture	16.74	16.56	16.18	10.3	11.0	13.11	13.65
Solid	83.26	83.44	83.82	89.7	89.0	86.89	86.35
Fat	1.63	2.07	1.84	0.9	2.0	0.88	1.75
Carbohydrate by dif-							
ference	71.28	65.44	72.42	74.1	72.0	77.15	70.44
Ash	2.47	4.73	0.22	1.3	4.1	1.01	1.81
Protein (N×6.25)	7.88	11.20	9.34	13.4	10.9	7.85	12.35

TOYO SAUCE.

This condiment is made principally by Chinese from soja beans,[16] *Glycine hispida* Maxim, imported from China. It is a Chinese sauce of the Worcestershire type. The process of manufacture varies in different localities in China, and in Manila different varieties and flavors are produced.

The beans are first boiled for about twelve hours, placed in baskets until the water has drained, and then transferred to earthenware jars. Salt brine, to about one-third of the bulk, is added, and spontaneous fermentation allowed to go on in the sun for from two to four months. (Plate V, fig. 2.) The fermented mass is again boiled for another twelve hours, and the clear liquid is bottled and sold under the name of the toyo sauce. Sometimes it is boiled two or three times producing different grades of strengths of sauce. Molasses or sugar are sometimes added, and this variety is called *si yao* (Chinese).

The Macao Chinese add a quantity of wheat flour to the boiled beans and dry the mixture in thin layers on trays several days before placing in jars for fermentation. This process hastens the fermentation.

The natives make a similar sauce from a European bean. The fermenting process is practically the same. After fermentation the mixture is boiled, and mustard, pepper, or other seasoning, and about one-third vinegar are added to the sauce. Analyses of 2 samples of toyo and 1 analysis of the molasses used in the manufacture of some varieties are given in the following table:

[16]For other foods made from soja beans see Gibbs and Agcaoili. *This Journal, Sec. A* (1912), 7, 47.

TABLE XVIII.—*Analyses of toyo sauce.*

Constituent.	Toyo.	Toyo made with sugar.	Crude molasses.
Solids	34.74	41.69	70.46
Volatile at 100°	65.26	58.31	29.54
Total	100.00	100.00	100.00
Protein (N × 6.25)	0.75	4.93	0.53
Acidity as acetic	0.00	1.68	0.00
Reducing sugars (invert sugar)	2.59	9.50	12.64
Sucrose	3.25		54.14
Ash	27.47	24.74	2.05
Sodium chloride	24.86	20.12	1.29
Alcohol		trace	
Undetermined, probably fat	.68	2.52	1.10

CHOCOLATE.

Chocolate is prepared for the local market in a number of small factories in the Philippine Islands. The majority of these establishments are run by Chinese, and the methods employed are the most crude. The roasted beans are pulverized by hand between stones. The stone used for crushing and mixing is shaped very much like a rolling pin with flat sides. (Plate VI.)

The standards adopted by the United States of America are as follows: [17]

c. COCOA AND COCOA PRODUCTS.

1. *Cocoa beans* are the seeds of the cacao tree, *Theobroma cacao* L.

2. *Cocoa nibs, cracked cocoa,* is the roasted, broken cocoa bean freed from its shell or husk.

3. *Chocolate, plain chocolate, bitter chocolate, chocolate liquor, bitter chocolate coatings,* is the solid or plastic mass obtained by grinding cocoa nibs without the removal of fat or other constituents except the germ, and contains not more than three (3) per cent of ash insoluble in water, three and fifty hundredths (3.50) per cent of crude fiber, and nine (9) per cent of starch, and not less than forty-five (45) per cent of cocoa fat.

4. *Sweet chocolate, sweet chocolate coatings,* is chocolate mixed with sugar (sucrose), with or without the addition of cocoa butter, spices, or other flavoring materials, and contains in the sugar- and fat-free residue no higher percentage of either ash, fiber, or starch than is found in the sugar- and fat-free residue of chocolate.

5. *Cocoa, powdered cocoa,* is cocoa nibs, with or without the germ, deprived of a portion of its fat and finely pulverized, and contains per-

[17] U. S. Dept. Agr., Office of the Secretary (1906), Circular No. 19, 17.

centages of ash, crude fiber, and starch corresponding to those in chocolate after correction for fat removed.

6. *Sweet cocoa, sweetened cocoa*, is cocoa mixed with sugar (sucrose), and contains not more than sixty (60) per cent of sugar (sucrose), and in the sugar- and fat-free residue no higher percentage of either ash, crude fiber, or starch than is found in the sugar- and fat-free residue of chocolate.

Leach [18] states that the most common adulterants of cocoa are sugar and various starches, and occasionally iron oxide and ground wood in the cheaper varieties.

A large proportion of the chocolate manufactured in Manila is adulterated by mixing with peanuts at the time of grinding. The Chinese manufacture a number of different grades of chocolate, and the grading and selling price are largely governed by the amount of peanuts used.

From a number of analyses made in this laboratory, the following are selected:

TABLE XIX.—*Analyses of chocolates found in the Manila market.*

	Constituent.								
	Mois-ture.	Fat.	Per-centage of pea-nut oil in fat. [a]	Pro-tein.	Ash.	Ash in-soluble in wa-ter.	Crude fiber.	Starch.	Sucrose.
Samples from native factories	3.77	48.00	none		3.71	1.70	3.40	10.26	
	2.89	29.9	none		2.34	1.23	1.60	6.20	38.99
	1.83	22.85	25.00						53.70
	1.10	22.40	20.00						60.20
	1.96	21.60	25.00						59.70
	1.88	23.42	46.00						61.40
	1.39	22.85	50.00						71.60
	1.10	20.00	9.00						59.38
	2.40	24.27	12.80	10.40	2.50				59.23
	3.38	18.34	13.00	7.64	1.84				59.24
Samples used by United States Army	2.05	36.75	none	6.50	3.00		1.85		22.00
	0.70	32.44	none	5.25	2.63		1.20		25.66

[a] Calculated from quantitative estimations of arachidic acid.

[18] Food Inspection and Analysis. London (1907), 305.

ILLUSTRATIONS.

PLATE I.

FIG. 1. Fish drying in the sun.

2. Interior of an establishment for smoking fish in Tondo, Manila. Smoke from saw-dust fires issues from the holes and passes through trays of fish.

PLATE II.

FIG. 1. A corral of ducks on the Pasig River at Pateros.

2. An incubating room for the making of balut. The bundles on the floor contain ducks' eggs ready for packing in the bamboo cylinders.

PLATE III.

FIG. 1. An incubator used for hatching ducks' eggs. The men are engaged in turning the eggs.

2. A bihon factory. The process of grinding the rice between the millstones is shown. On the left are the sacks of ground material from which water is draining.

PLATE IV.

FIG. 1. A bihon factory. Balls of dough are shown on the kneading table in the foreground. In the background on the right is the caldron of boiling water and the press in place over it. The heavy beam forms the lever which is drawn down upon the dough in the perforated box, by winding the rope upon the drum shown in the foreground on the right.

2. Misua (on the right) stretched upon sticks and mique (on the left) on frames exposed to the sun to dry.

PLATE V.

FIG. 1. Misua and mique drying. Mique and bihon have the same appearance in photographs.

2. The manufacture of toyo sauce. Soja beans fermenting in earthenware jars in the sun.

PLATE VI.

Interior of a chocolate factory in Manila.
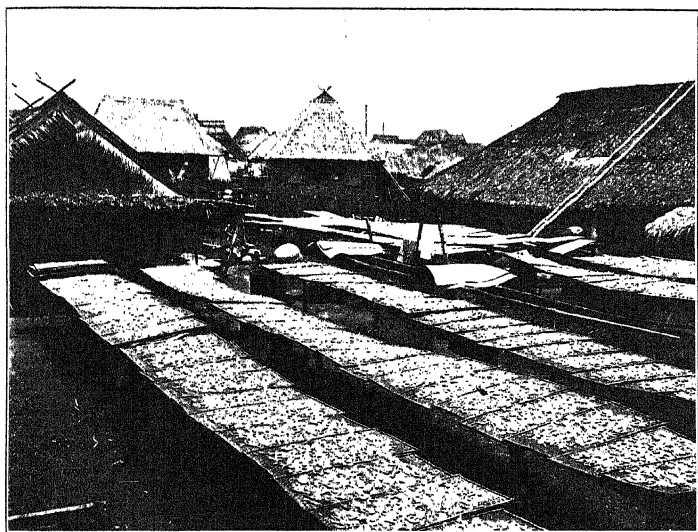
Fig. 1.　Fish drying in the sun.
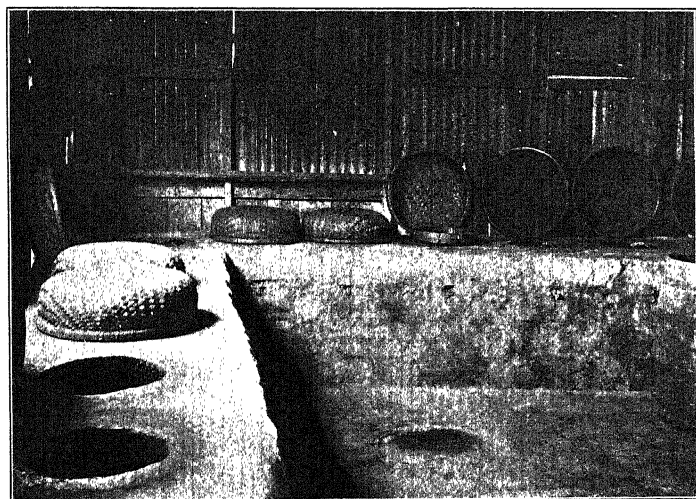
Fig. 2.　Establishment for smoking fish, Tondo, Manila.

PLATE I.
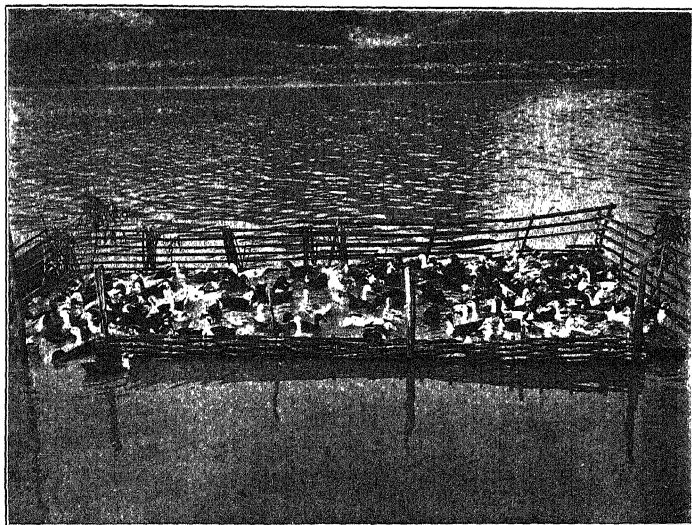
Fig. 1. A corral of ducks on the Pasig River at Pateros.

Fig. 2. An incubating room in a balut factory.

PLATE II.
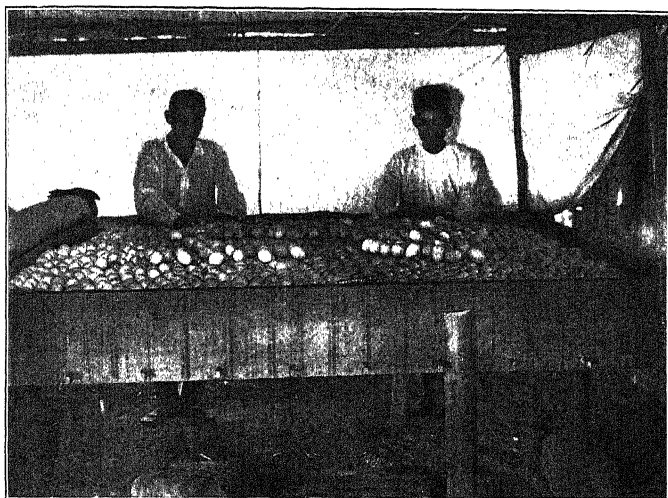
Fig. 1. An incubator used for hatching ducks' eggs. The men are engaged in turning the eggs.
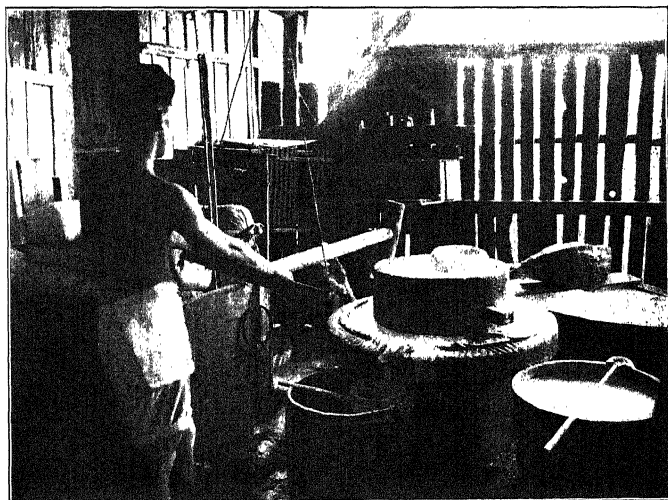
Fig. 2. A bihon factory. The process of grinding the rice between millstones is shown.

PLATE III.
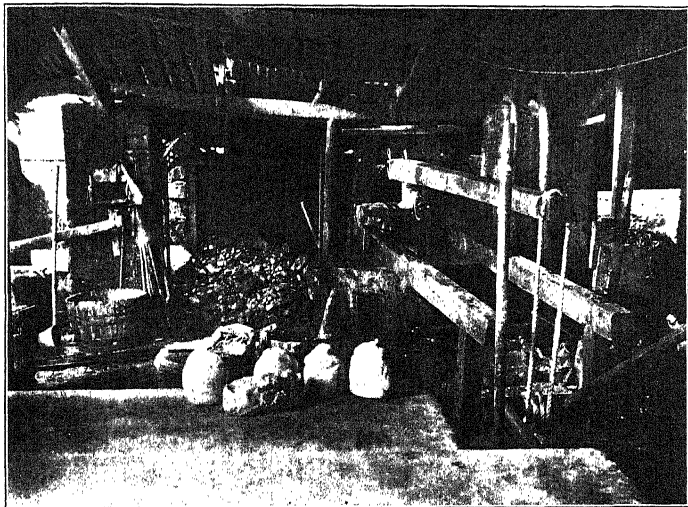
Fig. 1. A bihon factory. Balls of dough are shown on the kneading table in the foreground.
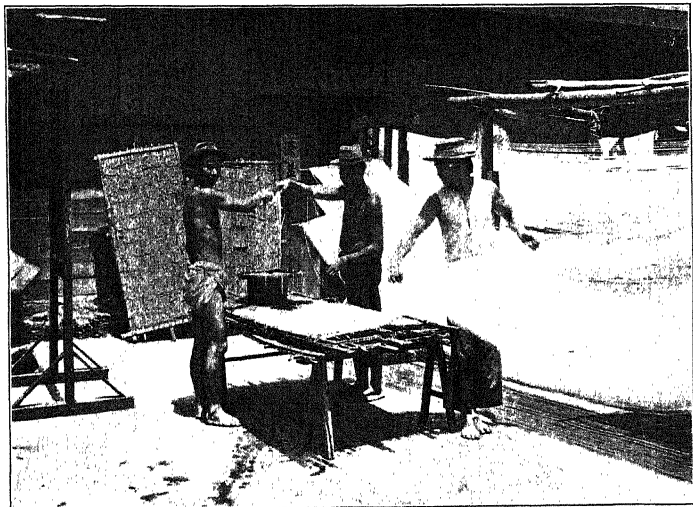
Fig. 2.   Misua (on the right) stretched upon sticks and mique (on the left) on frames
exposed to the sun to dry.

PLATE IV.
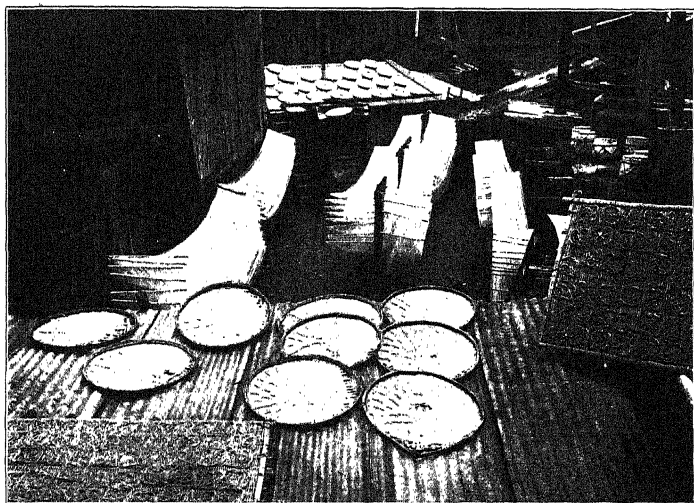
Fig. 1. Misua and mique drying.

Fig. 2. The manufacture of toyo sauce. Soja beans fermenting in earthenware jars.
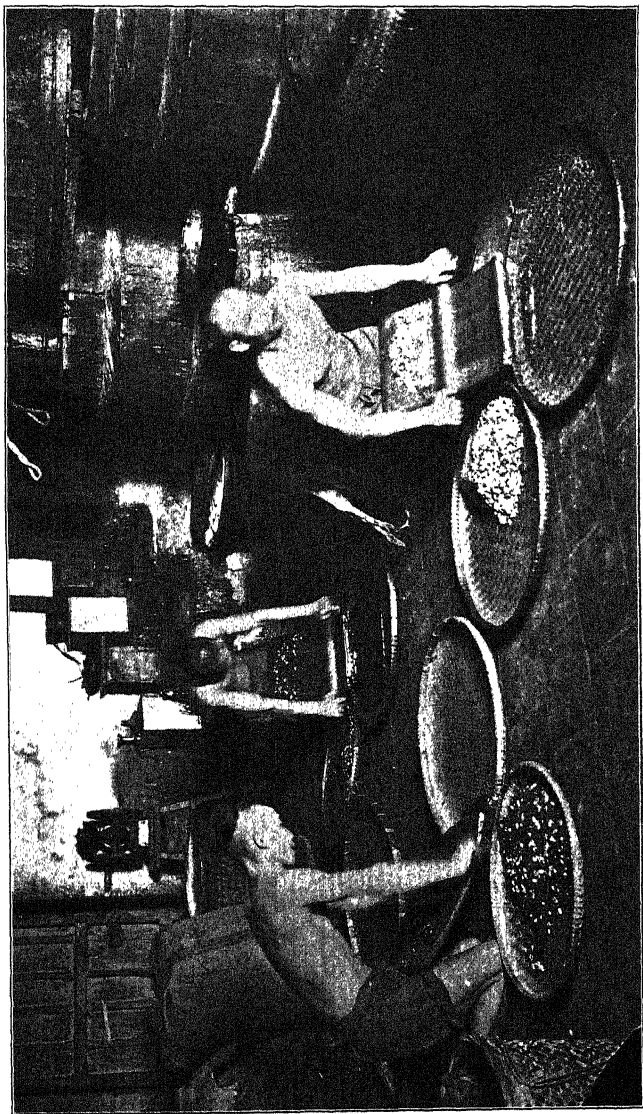
PLATE V.

PLATE VI. INTERIOR OF A CHOCOLATE FACTORY IN MANILA.

PHILIPPINE CITRUS-FRUITS: THEIR COMMERCIAL POSSIBILITIES AND A CHEMICAL STUDY OF A FEW OF THE MOST IMPORTANT VARIETIES.

By H. D. GIBBS[1] and F. AGCAOILI.

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

CONTENTS.

NARANJITA.   CALAMANSI.

CAJEL.   CALAMONDIN.

DAYAP (LIME).

The citrus-fruits of the Philippine Islands, tabulated by Wester and Barrett,[2] are:

Biasong, *Citrus* sp. A small, oblong, pyriform, very distinct fruit from others of the same genus, found in Cebu.

Cabuyao, *Citrus hystrix* DC. This tree is found in most municipalities, although usually in few numbers in each municipality; there are several varieties.

Calamondin, *Citrus mitis* Blanco, is quite generally distributed and the fruit may be found in the municipal markets throughout the year.

Citron, *Citrus medica* L. Rarely found except in the gardens of hacenderos.

Colo, *Citrus* sp. A rather large, pyriform fruit occurring in Cebu.

Lemon, *Citrus limonum* Risso. The lemon is grown to less extent even than the lime; in fact, it scarcely ever appears in the market; three distinct varieties occur.

Lime, *Citrus limetta* Risso.[3] The lime occurs in several varieties; the best of these is the "limon real," a rather large oblately flattened fruit, the better seedling trees of which produce a very superior fruit. The species is of general distribution throughout the Philippines but is less in evidence than the pomelo, mandarin, orange, and calamondin.

Mandarin, *Citrus nobilis* Lour. The most generally cultivated species in the genus. It is fairly well disseminated throughout the Islands but Batangas is the only province where its cultivation has assumed any importance. * * *

Orange, *Citrus aurantium* L. Fairly well distributed but of limited cultivation; grown principally in Batangas, Cuyo Islands and Pangasinan.

Pomelo, *Citrus decumana* L. Found more evenly distributed in the Archipelago than any other species of the genus, it is, however, never

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[1] Associate professor of chemistry, University of the Philippines.

[2] *Phil. Agr. Rev.* (1912), 5, 365.

grown extensively. Seedlings producing excellent fruit, some nearly seedless, have been found in several provinces.

Samuyao, *Citrus* sp. A small, nearly round fruit, conspicuously dented at the apex, growing in Cebu.

Sua,[1] *Citrus* sp. An oblately-flattened citrus fruit grown in Cebu and other parts of the Visayas, possibly a variety of *Citrus medica* L.

Messrs. Wester and Barrett inform us that these 12 forms represent only a small percentage of the total. The valid Philippine species, the natural hybrids, and the introduced species will total in the neighborhood of 100 more or less distinct forms. Mr. Merrill is of the opinion that various forms of *Citrus* found in the Philippines represent not more than 10 or 12 valid species from a botanical standpoint, possibly a less number than this.

Some of these fruits might be made commercially important, but up to the present time only one or two species of *Citrus* have been cultivated in quantities sufficient to make the crops worthy of note. Nothing has been accomplished in the improvement of species, and very little in the education or encouragement of the native growers, and as a natural consequence the few citrus-fruits upon the market leave much to be desired, and many of the existing orchards present dismal pictures of ignorance, mismanagement, and neglect. The Bureau of Agriculture is now working to remedy these conditions.

The following investigations were undertaken to determine the value of the most promising species and to develop methods for their utilization. The manufacture of oil from orange peel and of paper from the pulp, and the bottling of orange, lemon, and lime juice have been studied in addition to the chemical investigations of the fruit. As a result of our studies we believe that it will be possible to develop the production of orange-peel oil and the bottling of orange and lime juice upon a commercial basis, but not at the present time. No industry of this nature will prove profitable until the practical labor of improving the species and the orchards is accomplished.

THE ORANGE.

Naranjita (Spanish), *sintonis* (Tagalog), is a green loose-skinned orange of the Mandarin type, *Citrus nobilis* Lour., a form

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[1] Mr. E. D. Merrill, chief botanist of this Bureau, offers the criticism that the correct name for *lime* occurring in the Philippines is *Citrus lima* Lunan, *C. limetta* Risso being a synonym, and that *suha*, spelled *sua*, above, is a common name in Luzon for the pomelo.

described by Blanco as *Citrus reticulata*. (Plate IV, fig. 1.) It is the orange commonly found in the Manila market, and is grown to the greatest extent in the Province of Batangas.

Cruz [4] of the Bureau of Agriculture estimated, in 1909, that of the 10,017,800 oranges grown on 871 hectares in the Philippine Islands, Batangas Province produced 6,211,500 oranges from 547 hectares.

Mr. Higgins, president of the Manila Railroad Company, estimates shipments from Batangas Province for the past three years as follows:

Year.	Tons.	Calculated number of oranges.
1909	726	5,260,000
1910	8,000	58,000,000
1911	427	3,000,000

The low figures for 1909 are accounted for by the fact that this branch of the railroad was built in this year, prior to which large shipments were made by other means of land transportation (Plate III) and by water, and in 1911 by the great injury which the crop suffered from the ejecta from Taal Volcano,[5] a severe eruption of which occurred in January 30, 1911.

The crop for 1912, which is now coming into the market, gives every promise of being large, and the Manila Railroad Company anticipates a greater tonnage than in 1910, due in a large measure to the fact that their Batangas line is completed to the terminus. Tanauan station has so far furnished the greatest tonnage.

On August 9, 1912, one of us with Mr. E. D. Merrill, of this Bureau, made a trip of inspection through the orange groves of Batangas Province in the neighborhood of Santo Tomas and Tanauan. We found that the existing extensive groves were in very poor condition. The trees are planted too close to produce the best results, and apparently no attempt is made to prune or otherwise improve them. Cultivation is not followed to any extent, and consequently the general appearance of the orchards is unkempt and many are overgrown with bushes, which apparently are cut every year or two. (Plate I, figs. 1 and 2.) In young orchards cultivation between the rows of trees is followed, for growing corn or other crops.

[4] *Phil. Agr. Rev.* (1909), 2, 311.

[5] Pratt, *This Journal, Sec. A* (1911), 6, 63; Worcester, *Nat. Geog. Mag.* (1912), 23, 313.

No fungus diseases were observed, although some harmless fungi were found on twigs that had been killed by other causes. On some trees both plant lice and scale insects were abundant, and undoubtedly do much injury to the trees. Spraying, to kill these pests, is apparently never resorted to. In old trees much damage by borers, apparently the larvæ of some species of beetle, was observed, but this damage could readily be reduced to a minimum with a little care and attention on the part of the owners. A few trees suffering from gummosis were observed, but little information is at hand regarding its prevalence. (Plate II.) Nearly every tree observed was host of from one to many vigorous specimens of *Loranthus philippensis* Cham., a parasitic plant of the mistletoe family. This parasite must work a considerable amount of injury to the orchards, but could readily be exterminated by pruning. It is apparent that the average native does not appreciate the parasitic nature of this plant, for no attention is paid to it. (Plate II.) Our investigations of this fruit have been carried on for a period of almost three years, and they include two crops. The gross analysis of this orange is given in Table I, the chemical analyses of the juice in Table II, and an analysis of the pulp in Table III.

TABLE I.—*Gross analyses of naranjitas.*

Date.	Number of oranges.	Average weight of—			Average amount of juice.	Average number of seeds.	Average weight of seeds in one orange.
		Whole.	Peel.	Pulp.			
		Grams.	*Grams.*	*Grams.*	*Cc.*		*Grams.*
January 5, 1911	140	164	38	126			
January 5, 1911	36	170	38	132	ª 57		
January 5, 1911	102	165	38	127			
January 10, 1912	ᵇ100	142.23	32.33	110	ᶜ 66		
January 11, 1912	ᵈ100	119.69	27.04	92.65	ⁿ 52		
January 23, 1912	ᶠ300	102.3	26.6	ᵍ75.7	ʰ33.3		
January 23, 1919	10	102	25.6	76.4		22	4.2
Totals	788	138	32.2	106	52	22	4.2

ª This juice was expressed in a hydraulic press at 100 kilograms per square centimeter pressure. The analysis is given in Table II, column 1.

ᵇ Oranges of uniform size selected.

ᶜ Pressed in a hydraulic press at 100 kilograms per square centimeter pressure. The analysis is given in Table II, column 4.

ᵈ Not selected.

ᵉ Juice expressed by hand in cloth bags.

ᶠ The basket containing 300 oranges cost 6 pesos (3 dollars United States currency) or 2 centavos (1 cent) per orange.

ᵍ The analysis of the pulp is given in Table III.

ʰ The analysis of the juice is given in Table II, column 5. Fermentation experiments on this juice are described under the heading *orange brandy.*

From the data in Table I the average percentage gross composition of this variety of orange is:

Constituent.	Per cent.
Peel	23.4
Pulp and seeds	76.6
Seeds	3.0
Average weight of 788 oranges (grams)	138
Average number of seeds in each orange	22

The crop of 1913, which is at this time coming upon the market, is much below the average in size, and is an inferior product in every respect. This may be due partly to the immature condition of the fruit.

TABLE II.--*Chemical analyses of the juice of the naranjita from the crops of the years 1911 and 1912.*

Column	I.	II.	III.	IV.	V.
Date of analysis	Jan. 5, 1911. a	Jan. 11, 1911. b	Nov. 14, 1911. c	Jan. 10, 1912. d	Jan. 23, 1912.
Density 15°/15	1.0393		1.0388	1.0470	
Solids	9.40	9.90	9.12	10.93	11.80
Sucrose	4.21	7.00	4.18	5.19	7.11
Reducing sugars	4.17	2.00	2.92	4.58	3.44
Protein (N×6.25)			0.52	0.82	0.75
Ash	0.34	0.33	0.35	0.43	0.48
Citric acid	0.63	0.35	1.21	0.74	0.60

a A portion of this juice was bottled January 6, 1911, and sterilized by heating to 78° for two hours.

b This juice was centrifuged thirty minutes, 50 grams of sucrose to the liter added, filtered through Berkefeld filters, and bottled in sterile bottles.

c Juice from 10 average oranges purchased in the Manila market, expressed by gentle hand pressure. The high acidity and also the fact that the samples were purchased rather early in the season lead to the belief that the oranges were not ripe.

d A portion of this juice was bottled with and without the addition of 5-per-cent sucrose, and then sterilized by heat.

TABLE III.--*Analysis of pulp, January 23, 1912.*[a]

Constituent.	Per cent.
Solids	12.70
Sucrose	4.61
Reducing sugars	1.94
Protein (N×6.25)	1.19
Ash	1.36
Citric acid	0.53

Analysis of the ash of the pulp.	
NaCl	2.93
SO₄	2.52
K₂CO₃	85.75

a The analysis of the juice expressed from this pulp is found in Table II, column V.

Many analyses of oranges grown in various parts of the world are to be found in the literature [6] and for purposes of comparison the analyses of two well-known varieties are given in Table IV.

TABLE IV.—*Analysis of two varieties of California oranges.*

Name.	California Valencia.	California Washington navel.
	Grams.	*Grams.*
Weight of one orange	190	184 to 375
Shell	22.1	18.6 to 30.3
Juice:	*Per cent.*	*Per cent.*
Solids	11.40	12.40 to 15.20
Sucrose	9.20	10.10 to 12.55
Reducing sugars	4.90	9.94 to 5.86
Citric acid	1.12	0.066 to 1.68

BOTTLED ORANGE JUICE.

In order to determine if any special difficulties were to be encountered in the preservation of orange juice, and also its quality as a beverage, about 70 bottles, varying in capacity from 1 liter to 180 cubic centimeters, were filled, sterilized, and stored in the laboratory at room temperature, which averages about 30°. Sterilization was effected by placing the tightly stoppered bottles, the corks being wired, in a tank of water heated to 80°, for periods varying from forty-five minutes to two hours, and also, in some cases, by filtering through Berkefeld filters and bottling in sterile bottles without heating. Sucrose, in amounts varying from 5 to 15 per cent, was added to some of the samples before bottling. The breakage during sterilization was very low, and afterward was nil. In no case was there a failure to effect complete preservation. At this time some of the bottles have been in storage for two years.

At intervals during the storage period, bottles were opened, analyzed, and the opinion of a number of persons obtained regarding the flavor. The analyses are given in Table V and were always made upon the clear juice decanted from the sediment. These analyses show no changes other than those to be expected. The solids and nitrogen show slight decreases from the original analyses due to the removal of sediment, the sucrose is almost entirely inverted, and the acidity in some cases is slightly increased.

The flavor of the beverage is somewhat bitter; it is agreeable

[6] König: Chemie der menschlichen Nahrungs- und Genussmittel. Berlin (1903), 1, 842.

to some, and disagreeable to other, palates. This bitterness is greatly masked by the addition of sugar, and the samples containing 15 per cent of added sucrose were pronounced excellent by all who tried them. Much of the bitterness can be avoided by methods of pressing which will avoid, as much as possible, crushing the seeds and the segment covering. As a breakfast beverage this orange juice would undoubtedly find favor with discriminating consumers.

TABLE V.—*Analyses of naranjita juice after storage.*

Column No.	I.[a]	II.[b]	III.[c]	IV.[c]	V.[d]	VI.[e]
Date of analysis	Sept. 28, 1911.	Jan. 11, 1912.	Sept. 19, 1912.	Sept. 28, 1912.	Sept. 28, 1912.	Sept. 17, 1912.
Duration of storage	8 months 22 days.	1 year 6 days.	1 year 8 months 13 days.	1 year 8 months 22 days.	1 year 8 months 18 days.	1 year 8 months 7 days.
Density			1.0390	1.0383	1.0675	1.0470
Solids	13.03	12.82	8.61	8.83	14.69	10.79
Sucrose	3.81	0.00	1.54	0.60	2.92	1.71
Reducing sugars	8.39	11.46	6.39	7.12	9.98	7.25
Protein (N×6.25)	0.33	0.53	0.36	0.21	0.48	0.57
Ash	0.32	0.33	0.20	0.38	0.45	0.38
Acidity calculated as citric acid	0.49	0.80	0.39	0.46	0.70	0.82

[a] This juice was pressed on January 5, 1911, and the original analysis is given in Table II, column 1. Five per cent of sucrose was added, the juice securely corked in glass bottles and sterilized by heating for one and one-half hours at 80°. The state of preservation was perfect.

[b] This juice is the same as *a* after a longer storage period. The bottle showed a very slight pressure in opening.

[c] This juice is a portion of that pressed on January 5, 1911, and bottled without the addition of sucrose. On January 13, 1912, the bottles were opened and found to be in a perfect state of preservation. The clear juice was decanted from the sediment, rebottled, and sterilized by heating forty-five minutes to 78°.

[d] This juice is a portion of that pressed on January 10, 1912, to which 5-per-cent sucrose had been added before bottling. It was sterilized in the usual manner. The original analysis is given in Table II, column 4.

[e] This juice is the same as *d* without the addition of sucrose.

FERMENTATION OF ORANGE JUICE.

Two different lots of orange juice were fermented with the addition of yeast. The analyses of the original juice are given in Table II, columns IV and V.

The first lot fermented completely in seventy-two hours. After fermentation the juice contained 0.2 per cent reducing sugar and 5.58 per cent alcohol. A distilled beverage was made from this juice in the laboratory, by methods approximating those employed in the distillation of pot-still beverages. The flavor of this product was very good even while new, and on aging in wood for a short period it was much improved. The

analysis after aging in wood for sixty days is given in Table VI, column 2.

The second lot of orange juice, consisting of 10 liters from 300 oranges, was fermented and distilled in the same way. The analysis of this product is given in Table VI, column 1.

TABLE VI.—*Analyses of orange brandy.*[a]

Column No.	1.[b]	2.[c]
Density 17°.	0.9276	0.9480
Alcohol, per cent by volume	48.4	40.9
Solids	2.07	38.5
Total acids	122.2	51.0
Volatile acids	122.0	49.0
Esters	12.7	7.2
Aldehydes	30.4	0.0
Higher alcohols	121.0	124.0

[a] All values, except density and alcohol, are expressed as parts per 100 liters of 100 proof spirits.

[b] Analysis by A. H. Wells.

[c] Analysis by E. R. Dovey.

ORANGE OIL.

With M. V. Rosario.

The oil was extracted from the peel in the following manner. The peels were rubbed under water on a grater to disintegrate the oil cells, the liquid was then strained through muslin, and the pulp squeezed and washed with petroleum ether. The petroleum ether was added to the water, agitated, and separated. This was repeated with 3 portions of solvent. The petroleum ether portions were then united and evaporated under a pressure of 12 to 15 millimeters at a temperature below 50° until all of the solvent was expelled.

The yield together with the constants of the oil are given in Table VII.

TABLE VII.—*Orange oil from skins of naranjita.*

Lot No.	Number of oranges.	Average weight of peel.	Yield of oil 100 peels.	Density at 15°.	A$\frac{30°}{D}$.	N$\frac{30°}{D}$.	Ester number.
		Gms.	*Gms.*				
1	100			0.8416	+58°.90	1.456	13
2	300	2.712	19.33	0.8620	+83.39	1.470	7
3	300	2.561	14.00	0.8481	+78.97	1.468	10

The optical rotation is lower than that usually given for sweet orange oil, and yields given by Brooks[7] could not be equaled.

THE MANUFACTURE OF PAPER FROM ORANGE PULP.

With E. R. Dovey.

Since the pulp of this orange contains so much fiber, it occurred to us that, in the event of the establishment of a factory for bottling the juice, the pomace might be employed for paper making. The pomace was agitated with water and the seeds, which settled to the bottom, were readily removed. The pulp was then further disintegrated, a process not always necessary, and treated with bleaching powder. On passing through sieves of the proper mesh, a pulp of good character was obtained. Sheets of handmade paper produced from this stock were semitransparent and waterproof, and in appearance very much resembled a film of gelatine, although not so clear and transparent. Writing or printing is readily legible through the paper when placed in contact with it. In thin sheets the strength is very poor, and the paper is very brittle. Thicker sheets show a fair strength. At present we do not consider the product of value; however, it is possible that, owing to the waterproof and semitransparent properties, special use might be found for this paper. The analysis is as follows:

TABLE VIII.—*Analysis of orange-pulp paper.*

Constituent.	Per cent.
Moisture	10.7
Ash	3.4
Wax (ether extract)	15.7
Nitrogen	1.17
Protein ($N \times 6.25$)	7.3
Cellulose and undetermined	62.9

Cajel, or *dalandan,* is a yellow tight-skinned, sour orange, *Citrus aurantium* L., var. It is grown in Batangas Province to a lesser extent than the *naranjita,* and the remarks concerning the groves of the latter apply equally well to the *cajel.* Analyses of different lots of juice are given in Table IX.

[7] *This Journal, Sec. A* (1911), 6, 348.

TABLE IX.—*Analysis of the juice of the cajel orange.*

	Jan. 11, 1911. [a]	Nov. 14, 1911. [b]	Oct. 6, 1912. [c]
Density 15°/15°.	1.0284	1.0360	1.0160
Solids	6.91	7.88	6.18
Sucrose	3.75	3.03	1.55
Reducing sugars	2.33	2.47	3.34
Protein (N × 6.25)		0.57	0.22
Ash	0.34	0.45	0.31
Citric acid	0.29	1.80	0.32

[a] Juice from 10 average oranges. This juice was filtered through Berkefeld filters and bottled in sterile bottles.

[b] Juice from 12 average oranges.

[c] Analysis of the juice bottled as described under *a*, after a storage period of about one year and eight months. The state of preservation was perfect.

This variety of orange is so inferior to the naranjita in every respect that we see no future for it unless it is improved.

THE LIME.

Dayap, the common Tagalog name for the lime, *Citrus lima* Lunan, is a true lime which is grown only in small quantities in the Philippines. It is a fruit of good quality, and, when available in quantities, will be comercially valuable. (Plate IV, fig. 2.)

The cost of the limes in the Manila market is about 1 centavo each. When pressed by hand each one yields about 7 cubic centimeters of juice. A number of bottles of this juice were preserved by heating between 60° and 70° in the manner described under the naranjita orange and it was found to keep perfectly and retain its flavor. All persons who have tasted this bottled juice pronounce it excellent and superior to imported bottled lime juice.[8]

[8] Almost all of the lime juice heretofore offered for entry in the Philippine Islands has been found to contain excessive quantities of sulphurous acid.

The analyses are given in Table X.

TABLE X.—*Analyses of limes and lime juice. Average of 225 fruits.*

Unit.	Grams.
One fruit	44.
Peel of 1 fruit	7.36
Pulp of 1 fruit	36.6
Seeds in 1 fruit	1.

Date of analysis	Feb. 10, 1912.	Feb. 10, 1912.	Feb. 14, 1912.	Oct. 3, 1912.
Portion of fruit	Pulp.	Juice un-racked.	Juice racked.	Juice after steri-lization and stor-age for 8 months.
	Per cent.	Per cent.	Per cent.	Per cent.
Solids	12.37	9.05	8.83	8.33
Sucrose	0.00	0.00	0.00	0.00
Reducing sugars	0.50	0.50	0.36	0.02
Protein	0.94	0.58	0.48	0.36
Ash	0.66	0.35	0.35	0.37
Citric acid	4.24	7.77	7.77	7.38
Density			1.0380	1.0390
Ash:				
K2CO3	65.69			
NaCl	1.34			
Sulphates as H2SO4	3.47			

CALAMANSI AND CALAMONDIN.

Both *Calamansi* (Tagalog) and *Calamondin* (Tagalog) are apparently forms of *Citrus mitis* Blanco.   (Plate V.)

The analyses of these fruits are given in Table XI.

A large number of bottles of the juice of the kalamansi were sterilized in the manner previously described and were found to keep perfectly.   The flavor of the juice is not as agreeable as that of the lime.   Analyses after storage are given in Table XI.

TABLE XI.—*Analyses of calamansi and calamondin.*

Average—					Cala-mansi.	Cala-mondin.
Weight of each fruit (grams)					30	10
Weight of peel (grams)					6	2.2
Weight of pulp (grams)					24	7.8
Weight of seeds (grams)						1.6
Volume of juice (cc)					5	
Cost (peso)					0.004	0.002

	Calamansi.				Calamondin.	
Date of analysis	Jan. 25, 1912.	Jan. 25, 1912.	Oct. 3, 1912.		Feb. 15, 1912.	Feb. 16, 1912.
Portion of fruit	Pulp.	Juice un-filtered and viscous.	After sterilization and storage 8 months.		Pulp.	Juice.
			Not racked.	Racked.		
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Solids	11.55	8.77	8.87	8.89	14.24	10.33
Sucrose	0.68	0.68	0.04	0.03	0.00	0.00
Reducing sugars	1.67	1.79	1.74	2.39	0.41	0.53
Protein	0.83	0.53	0.36	0.35	1.40	0.01
Ash	0.56	0.24	0.49	0.59	0.68	0.62
Citric acid	4.94	5.64	5.59	5.53	4.79	5.52
Density				1.0450		
Ash:						
NaCl	2.53					
K2CO3	84.36					
Sulphates as H2SO4	2.89					

ILLUSTRATIONS.

PLATE I.

Fig. 1. Grove of naranjita trees near Tanauan, Batangas Province. The lack of pruning is very evident. The dense undergrowth indicates very lax culture methods. (Photograph by Gibbs.)

2. Orange tree near Tanauan. (Photograph by Chas. Storms, Bureau of Education.)

PLATE II.

Orange grove near Santo Tomas, Batangas Province. Mount Maquiling in the distance. This grove is practically ruined by gummosis, attacks of scale insects, and boring beetles. (Photograph by Gibbs.)

PLATE III.

Method of transporting oranges to market. Before the completion of the railroad into the orange district, almost all of the oranges were marketed in this way. (Photograph by Gibbs.)

PLATE IV.

(Photograph by Cortes.)

Fig. 1. Naranjita.
2. Lime, dayap.

PLATE V.

(Photograph by Cortes.)

Fig. 1. Calamansi.
2. Calamondin.

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Fig. 1. Grove of naranjita trees near Tanauan, Batangas.
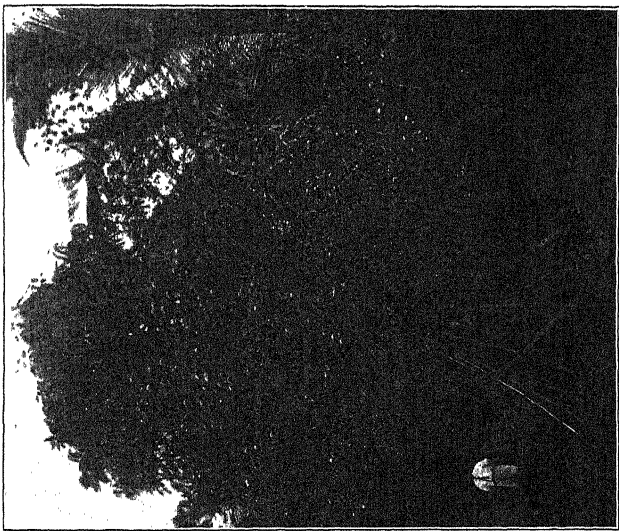
Fig. 2. Orange tree near Tanauan, Batangas.
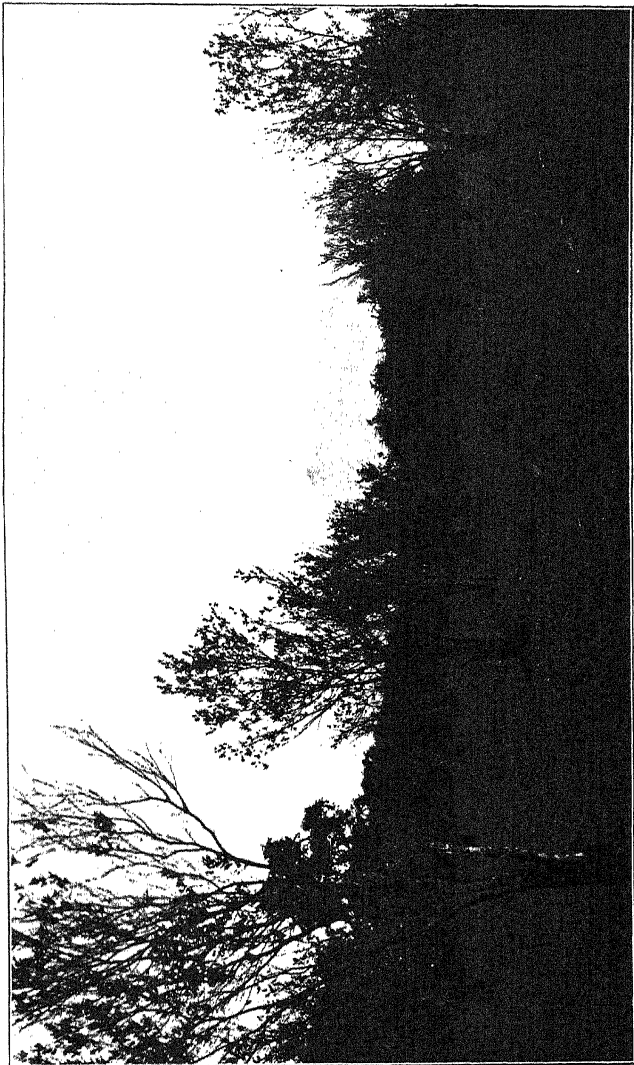
PLATE I.

PLATE II. ORANGE GROVE NEAR SANTO TOMAS, BATANGAS, INJURED BY GUMMOSIS, SCALE INSECTS, AND BORING BEETLES.
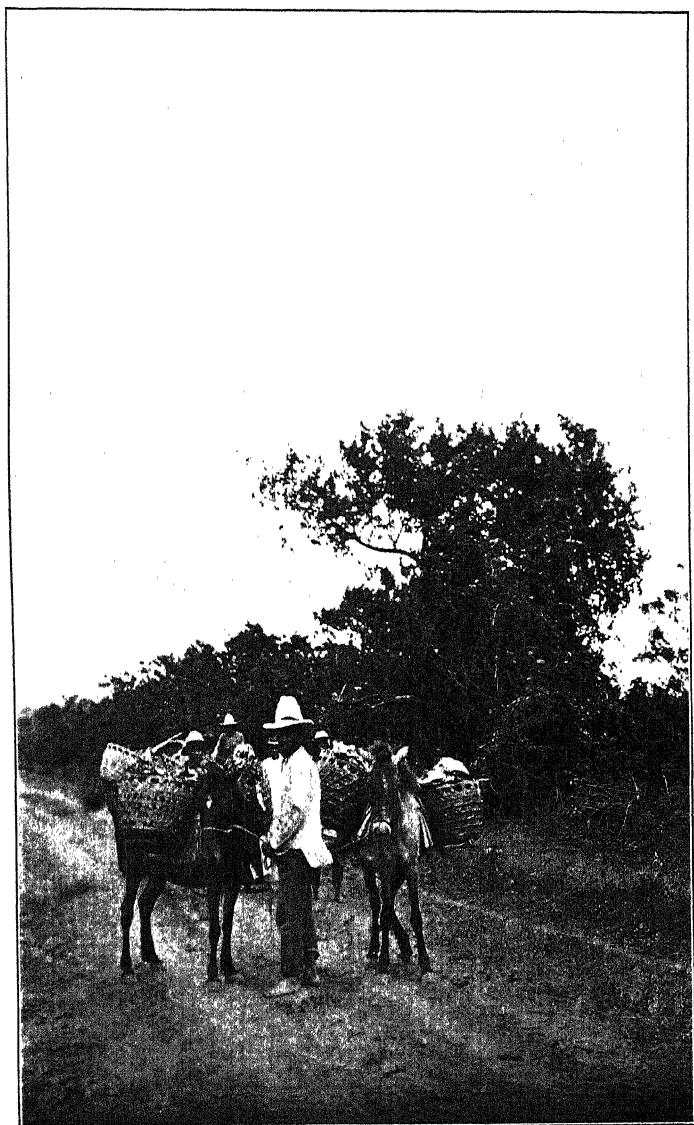
PLATE III. METHOD OF TRANSPORTING ORANGES TO MARKET.
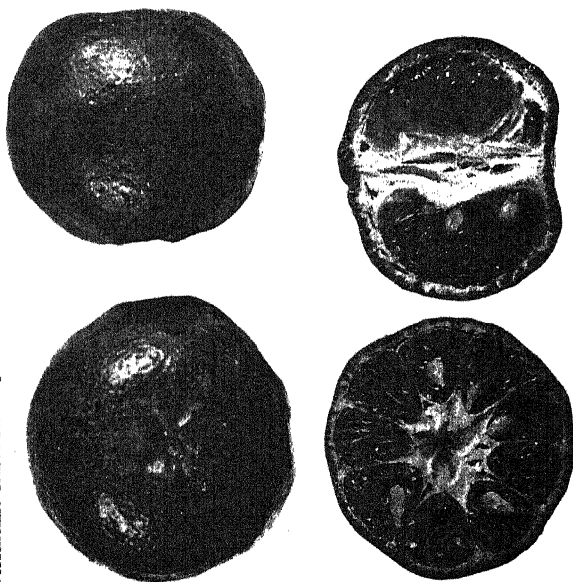
Fig. 1. Naranjita.
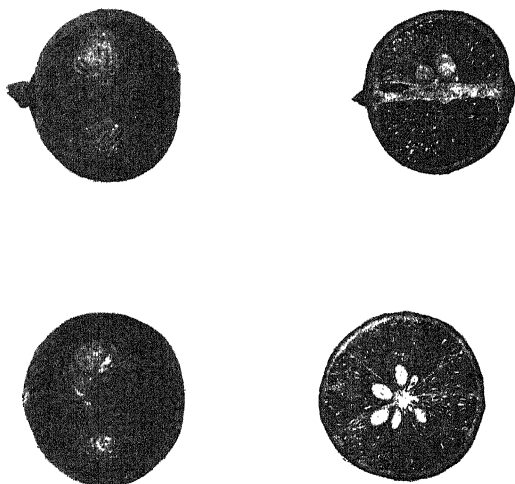
Fig. 2. Lime, dayap.

PLATE IV.
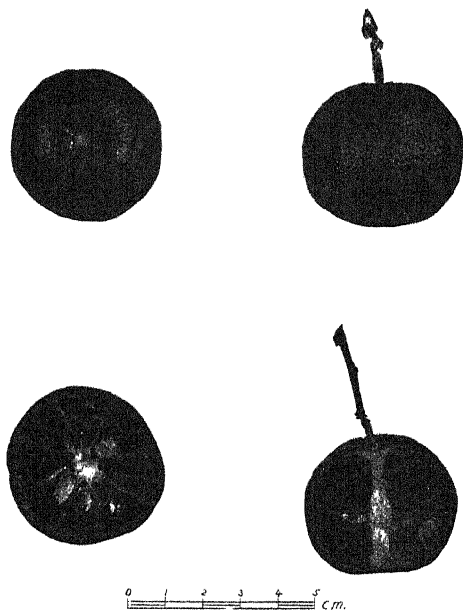
Fig. 1. Calamansi.

Fig. 2. Calamondin.

PLATE V.
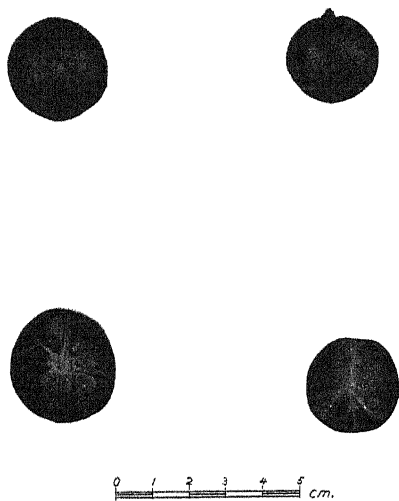
EDITORIAL.

A NEW TYPE OF LABORATORY CONDENSER FOR USE WITH VOLATILE LIQUIDS IN TROPICAL LABORATORIES.

During the course of some recent work on copra, in which it was desirable to obtain the oil by continuous extraction with ether, difficulty was experienced in obtaining efficient condensation of the ether vapor in the extractor. The apparatus employed was an ordinary Soxhlet extractor, having ground-glass joints, and fitted with a 4-bulb glass single-surface condenser. The source of heat was a 32-candlepower electric bulb placed below the extractor flask.

When the apparatus was allowed to run in the usual way, a considerable loss of ether was experienced. Even when water at the usual temperature of 30° was flowing through the condenser at the rate of 4,000 cubic centimeters per minute, the loss frequently amounted to 100 cubic centimeters per hour. Apart from the question of cost, such an escape of ether vapor was liable to cause fire or explosion in the vicinity of the extractor.

The particular problem to which reference has been made above; namely, of estimating oil in copra, might easily have been solved by employing a less volatile solvent, such as chloroform, but for the fact that it was very desirable to obtain figures comparable with others previously obtained, using ether as the solvent. With this object in view, a new type of laboratory condenser was designed for either the distillation or refluxing of volatile liquids. It depends upon the absorption of heat obtained by rapidly evaporating a liquid by means of an air blast. The adjoining diagram shows a vertical section of the condenser of approximately one-third scale.

The apparatus is constructed almost entirely of metal, the inner condensing surface being made of thin copper, the remainder of brass. The inner tube is enlarged into 3 circular chambers, divided into an upper and a lower portion by means of a disk of copper. The latter is provided with 4 apertures near the circumference, so that vapor can pass from the lower portion of the chamber to the upper. The space between the inner tube
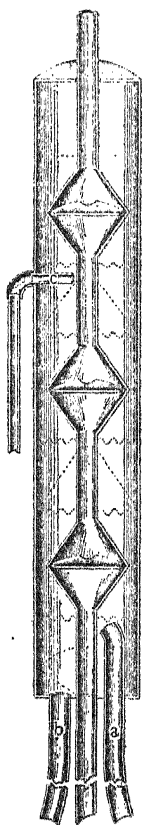
Fig. 1.

and the outer shell of thick brass is fitted with alternate cones, and corrugated disks of brass-wire gauze.

When the condenser is in operation, the air blast enters through tube A, the upper portion of which is bent so as to direct the blast toward the center of the first condensing chamber. Water is allowed to drip from tube C at the rate of approximately 6 cubic centimeters per minute. The corrugated disks receiving the heat from the inner tube by conduction become covered with a film of water which is rapidly evaporated by the air blast, the heat being thus absorbed. Any excess of water in the condenser runs to the bottom and is drained away by tube B. The wire-gauze cones constantly deflect the air blast toward the central heated surfaces, while the inverted cone at the bottom of the apparatus prevents the air blast from turning downward and escaping by tube B.

When supplied with 6 cubic centimeters of water and 120 liters of air per minute, the apparatus may be fitted to an extractor and run hermetically sealed. Under these conditions, 200 liters of ether vapor per hour may easily be condensed without any excess of pressure being observed.

This condenser has been found to be very efficient and convenient, and, in laboratories situated in the Tropics and provided with an air blast, should prove useful for a variety of purposes.

ERNEST R. DOVEY.

ILLUSTRATION.

REVIEW.

Like practically everything else which has been published in English on the coconut, with the exception of the results of scientific studies, this book is essentially a compilation. The work is somewhat of a unit, and has been performed with much more care than was used in the preparation of the best-known previous compilations on the subject. Nevertheless, it does not bear the stamp of experience in the field so much as of industry in culling the recent literature in the English language. Even in their notes on the extracts from other writers, the authors have not always been fortunate. For instance, it is twice explained that *Rynchophorus ferrugineus* is a small black insect.

However, the digestion of the literature has on the whole been well done. The authors have been endowed with common sense if not intimate familiarity with the coconut, and the advice they give as to the selection of land and the treatment of the crop is uniformly good. They have evidently been in the closest touch with manufacturers of coconut products and of apparatus and machinery incidental to the coconut business, and this side of the work is accordingly very full. There are also chapters and digressions on health and sanitation in the Tropics which are not without value to the older resident and should be useful indeed to the emigrant.

The most unfortunate feature of the book is the lack of attention to works published in French, German, and Dutch. Prudhomme's monograph on the coconut, which still remains decidedly the finest work on the subject in any tongue, seems not even to be mentioned.

E. B. C.

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